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(54) 【発明の名称】 R-Fe-B系希土類永久磁石材料

(57) 【要約】

【解決手段】 主相成分である $Fe_{14}R_2B_1$ 相 (但し、Rは少なくとも1種の希土類元素を示す) の存在容量割合が87.5~97.5%であり、希土類又は希土類と遷移金属の酸化物の存在容量割合が0.1~3%である R-Fe-B系磁石合金において、該合金の金属組織中に主成分としてZrとBとからなるZrB化合物、NbとBとからなるNbB化合物、及びHfとBとからなるHfB化合物から選ばれる化合物が、平均粒径5 μ m以下で、かつ上記合金中に隣り合って存在するZrB化合物、NbB化合物、及びHfB化合物から選ばれる化合物間の最大間隔が50 μ m以下で均一に分散していることを特徴とするR-Fe-B系希土類永久磁石材料。

【効果】 本発明によれば、高特性のR-Fe-B系希土類永久磁石材料を得ることができる。

【特許請求の範囲】

【請求項1】 主相成分である $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相（但し、Rは少なくとも1種の希土類元素を示す）の存在容量割合が87.5～97.5%であり、希土類又は希土類と遷移金属の酸化物の存在容量割合が0.1～3%であるRFeB系磁石合金において、該合金の金属組織中に主成分としてZrとBとからなるZrB化合物、NbとBとからなるNbB化合物、及びHfとBとからなるHfB化合物から選ばれる化合物が、平均粒径 $5\mu\text{m}$ 以下で、かつ上記合金中に隣り合って存在するZrB化合物、NbB化合物、及びHfB化合物から選ばれる化合物間の最大間隔が $50\mu\text{m}$ 以下で均一に分散していることを特徴とするR-Fe-B系希土類永久磁石材料。

【請求項2】 粒径 $100\mu\text{m}$ 以上の $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の巨大異常成長粒が、金属組織全体に対する存在容量割合で3%以下である請求項1記載の永久磁石材料。

【請求項3】 磁気特性がBrで12.5G以上、保磁力 iH_c が10kOe以上、角型比 $4 \times (BH)_{\max} / Br^2$ が0.95以上である請求項1又は2記載の永久磁石材料。

【請求項4】 RFeB系磁石合金が、重量百分率で、R27～33%（但し、Rは希土類元素の1種又は2種以上を示すが、Ndを15～33%含有する）、Co0.1～10%、B0.9～1.5%、Al0.05～1.0%、Cu0.02～1.0%、Zr、Nb及びHfから選ばれる元素0.02～1.0%、C0.03～0.1%、O0.05～0.5%、N0.002～0.05%、並びに残部がFe及び不可避の不純物からなる請求項1、2又は3記載の永久磁石材料。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、R-Fe-B系希土類永久磁石材料に関する。

【0002】

【従来の技術及び発明が解決しようとする課題】希土類永久磁石は、優れた磁気特性と経済性のため電気・電子機器の分野で多用されており、近年益々その高性能化が要求されている。これらの希土類永久磁石の内、R-Fe-B系希土類永久磁石は、希土類コバルト磁石に比べて主要元素であるNdがSmより豊富に存在すること、Coを多量に使用しないことから原材料費が安価であり、磁気特性も希土類コバルト磁石を遥かに凌ぐ極めて優れた永久磁石材料である。

【0003】このため、かかるR-Fe-B系希土類永久磁石の更なる高特性化が望まれている。R-Fe-B系希土類永久磁石を高特性化するためには、合金中の酸素濃度を低下させることが必要である。しかし、合金中の酸素濃度を低下させると焼結工程において異常粒成長が起こり易く、Brは高いが、 $(BH)_{\max}$ の不十分な角型性の悪い磁石となる。

【0004】本発明は上記事情に鑑みなされたもので、合金中の酸素濃度を低下させても、異常粒成長が少なく、高性能なR-Fe-B系希土類永久磁石材料を提供することを目的とする。

【0005】

【課題を解決するための手段及び発明の実施の形態】本発明者は、上記目的を達成するため鋭意検討を行った結果、Co、Al、Cu、それにZr、Nb又はHfを含有するR-Fe-B系希土類永久磁石中に微細なZr化合物、Nb化合物又はHf化合物を均一に分散して析出させることにより、主に低酸素工程で製造するNd系磁石合金の粒成長を抑制し、磁気特性と焼結温度幅を著しく改良した焼結永久磁石材料を得ることに成功した。

【0006】更に詳述すると、R-Fe-B系希土類永久磁石において、合金中の酸素濃度を低下させると異常粒成長が起こり易く、最適焼結温度幅も狭く、生産性が極めて悪い。そこで、上記問題解決のため新たな元素を合金に微量添加し、問題解決を試みた。

【0007】即ち、本発明者は、先に提案した特開2000-234151号公報で述べた通り、Cuを含むR-Fe-B系希土類永久磁石において新たに加える添加元素とその量を鋭意研究した結果、Zrを微量に添加することにより、残留磁束密度(Br)を若干上昇させ、保磁力(iH_c)を大幅に増加させることが可能であることを報告したが、更に磁気特性の向上を図るために製造工程中の酸素濃度の低減に努めたところ、ZrB化合物、NbB化合物又はHfB化合物を磁石中に微細かつ一様に析出させることによって、最適焼結温度領域を著しく拡大できることを知見し、本発明を完成させたものである。

【0008】以下、本発明につき更に詳しく説明する。本発明のR-Fe-B系希土類永久磁石材料（但し、Rは、希土類元素の1種又は2種以上を示す。）は、主相成分である $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の存在容量割合が87.5～97.5%であり、希土類又は希土類と遷移金属の酸化物の存在容量割合が0.1～3%であるRFeB系磁石合金において、該合金の金属組織中に主成分としてZrとBとからなるZrB化合物、NbとBとからなるNbB化合物、及びHfとBとからなるHfB化合物から選ばれる化合物が、平均粒径 $5\mu\text{m}$ 以下で、かつ上記合金中に隣り合って存在するZrB化合物、NbB化合物、及びHfB化合物から選ばれる化合物間の最大間隔が $50\mu\text{m}$ 以下で均一に分散していることを特徴とする。

【0009】上記RFeB系磁石合金について述べると、RFeB系磁石合金の磁気特性は、磁性を発現する $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の存在容量割合を増大させ、それに反比例して非磁性のRリッチ粒界相を少なくすることで、残留磁束密度とエネルギー積の向上が図られてきている。Rリッチ相は、主相 $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の結晶粒界をクリーニングし、粒界の不純物や結晶欠陥を取り除くことによ

って保磁力を発生させるという役割を担っている。従って、いくら磁束密度が高くなるからといって、磁石合金の組織中から完全にRリッチ相をなくすることはできず、少量のRリッチ相をできるだけ効率的に活用して粒界のクリーニングを行わせ、いかに大きな保磁力を得るかが磁気特性開発上の要点となる。一般に、Rリッチ相は活性であるため、粉碎や焼結工程などを通して容易に酸化し、R酸化物相を形成してRリッチ相を消耗してしまう。そして、少量に調整されたRリッチ相が、工程中で酸素と反応し、酸化物として消費されると、粒界組織の健全化が完全に行えず、所定の保磁力が得られなくなる。残留磁束密度の高い保磁力の大きな高性能磁石を得る、言い換えれば最少量のRリッチ相を有効に利用して磁気特性を得るには、製造工程を通してRリッチ相の酸化を防ぐ対策が必要となる。このため最新の高特性Nd磁石製造ラインでは、粉碎、成型、焼結の各工程を完全に酸素から遮断した状態で行い、非磁性のNdリッチ相及びNdの酸化物を極力少なくすることによって、磁性相 $\text{Fe}_{14}\text{Nd}_2\text{B}_1$ の量をできるだけ多くし、磁気特性の向上が図られる。

【0010】しかし、このような酸化反応防止によるNd酸化物相存在量の減少は新たな問題を引き起こす。それは、焼結工程での異常成長粒の発生である。

【0011】焼結工程では、微粉の焼結反応によって高密度化が進行する。成型された微粉は焼結温度で互いに接合しながら拡散し、介在する空孔を外部に排除することによって焼結体中の空間を充填し、収縮する。このとき共存するNdリッチな液相が焼結反応をスムーズに促進するといわれている。

【0012】焼結の後期段階において、焼結体は最終的な密度に到達すべく残存する空孔を系外に拡散させ排斥する。この最終的な密度向上と同時に、焼結の完了した各結晶粒がオストワルド成長によって成長し始める。各結晶粒が有する粒界はそれ自身が格子欠陥であって、成長によって体積当たりの粒界長さが小さくなると、粒界の持つ界面エネルギーが減少し、焼結体全体の自由エネルギーが低下して安定となる。

【0013】焼結Nd磁石のような磁壁ニュークリエーション型磁石の場合、結晶粒の大きさが小さいほど一般に保磁力は大きくなるので、できるだけ結晶粒の小さい焼結体が好ましい。結晶粒が大きくなるに従って保磁力が小さくなるのは、結晶成長して粒当たりの粒界面積が増大すると、低磁場で磁壁発生が可能となる重大格子欠陥の存在確率が高くなるためと考えられる。

【0014】格子欠陥にあまり影響を受けなくなるNd磁石の単磁区粒径約0.3 μm 程度まで結晶粒が小さくなるほどNd磁石の保磁力は高くなると予測されるが、現状では粉碎方法や微粉の安定性、焼結条件などの制約により、希土類焼結磁石では平均粒径で数 μm 、小さくても2 μm 程度の焼結体平均粒径が限界と考えられる。

【0015】上述したように、焼結工程の後期において、焼結体は、最終的な高密度化が進行すると共に、結晶粒の成長が起こる。磁石の磁束密度向上のために高密度化は必要であるが、保磁力の維持のためには結晶粒の成長は防止されなければならない。従来のNd磁石においては、一定量のNd酸化物が粒界の3重点などに介在物として存在していた。このNd酸化物が、結晶成長に伴う粒界移動をピン止めし、焼結体の密度化は進んでも、粒界の移動即ち結晶粒の成長は抑えることができた。

【0016】しかし、Ndの含有量を少なくし、更に工程での酸化を抑えた高特性Nd磁石においては、Nd酸化物の存在量不足のためにピン止め効果を十分に発揮することができなくなる。このため、特定の結晶粒が焼結温度で急激に大きく成長してしまう巨大異常成長粒発生の現象が現れる。その例を図20(a), (b)の顕微鏡写真に示すが、このように異常成長した結晶粒は、もともとの配向方向の結晶粒が大きくなる場合と、配向方向とは異なった方向の結晶粒が成長する場合がある。

【0017】図20(a), (b)においてアンカー効果による磁区が観察されているが、180度磁壁の方向が異常成長粒ごとに異なっており、配向の乱れていることが理解される。配向は変わらないが粒の大きくなってしまった結晶粒は保磁力が減少しており、配向も乱れてしまった粒では保磁力に加えて残留磁束密度も減少している。結果的に、得られる磁石のヒステリシス曲線は角型性の悪い、劣悪な磁気特性となる。

【0018】この高特性磁石製造における問題点を、本発明者は、主成分としてZrとBからなるZrB化合物、NbとBとからなるNbB化合物、HfとBとからなるHfB化合物から選ばれる化合物を、その析出平均粒径として5 μm 以下で、かつまた合金中に隣り合って析出する最大の間隔が50 μm 以下で均一に分散させることによって解決した。即ち、このようなZrB化合物、NbB化合物、又はHfB化合物の均一な分散により、焼結体の粒成長を極めて効果的に抑えることができた。ZrB化合物、NbB化合物、HfB化合物の粒界ピン止め効果は、5 μm 以下の小さな大きさであってもR酸化物と同等以上の効果を持ち、これを隣り合って析出する最大の間隔が50 μm 以下で均一に分散させることによって、R酸化物より少ない量で有効に粒成長を抑えることができる。このようなZrB化合物、NbB化合物、HfB化合物の効果によって、広い焼結温度範囲において巨大異常成長粒の発生を抑制することが可能となり、粒径が100 μm 以上となっている $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の巨大異常成長粒を金属組織全体に対して存在容量割合で3%以下とすることができる。

【0019】以上のように、本発明の希土類永久磁石材料は、主相成分である $\text{Fe}_{14}\text{R}_2\text{B}_1$ 相の存在容量割合が87.5%から97.5%であって、かつまた希土類又

は希土類及び遷移金属からなる酸化物の存在容量割合が0.1%から3%である高特性RFeB系磁石合金において、該合金の金属組織中に主成分としてZrとBとからなるZrB化合物、NbとBとからなるNbB化合物、及びHfとBとからなるHfB化合物から選ばれる化合物が、その析出平均粒径としては5 μ m以下で、かつまた上記合金中に隣り合って析出する最大の間隔が50 μ m以下で均一に分散しているものであり、この場合、この希土類永久磁石材料において、粒径が100 μ m以上となっているFe₁₄R₂B₁相の巨大異常成長粒が、金属組織全体に対して存在容量割合で3%以下であることが好適である。

【0020】ここで、上記希土類永久磁石合金は、その組成として、重量百分率で、

R=27~33%、特に28.8~31.5%

Co=0.1~10%、特に1.3~3.4%

B=0.9~1.5%、特に0.95~1.15%

Al=0.05~1.0%、特に0.1~0.5%

Cu=0.02~1.0%、特に0.05~0.3%

Zr, Nb及びHfから選ばれる元素=0.02~1.0%、特に0.05~0.3%

C=0.03~0.1%、特に0.03~0.08%

O=0.05~0.5%、特に0.05~0.45%

N=0.002~0.05%、特に0.002~0.04%

Fe=残部

更に、不可避の不純物からなるものであることが好ましい。

【0021】ここで、Rは希土類元素のうち1種又は2種以上であることを示すが、好ましくはPr, Nd, Tb, Dy, Hoの中から選ばれ、Ndを主成分に含有することが好ましい。特に合金組成中、Ndを15~33wt%、特に18~33wt%含有することが好ましい。この場合、Rは上述したように27~33wt%含有するが、これが27wt%未満ではiHcの減少が著しくなるおそれがあり、33wt%を超えるとBrの減少が著しくなるおそれがあるため、27~33wt%とすることがよい。

【0022】本発明においてFeの一部をCoで置換することは、Tc(キュリー温度)改善効果の上で有効であるが、Coが0.1wt%未満ではTc改善の効果が少なく、コスト面を考慮して0.1~10wt%とすることがよい。

【0023】Bは、0.9wt%未満ではiHcの減少が著しくなるおそれがあり、1.5wt%を超えるとBrの減少が著しくなるおそれがあるため、0.9~1.5wt%とすることがよい。

【0024】Alは、コストをかけずに保磁力(iHc)を上昇させる上で有効であるが、0.05wt%未満ではiHcの増加の効果が非常に少なく、1.0wt

%を超えるとBrの減少が大きくなるおそれがあるため、0.05~1.0wt%とすることがよい。

【0025】Cuは、0.02wt%未満ではiHcの増加の効果が非常に少なく、1.0wt%を超えるとBrの減少が大きくなるおそれがあるため、0.02~1.0wt%とすることがよい。

【0026】Zr, Nb及びHfから選ばれる元素は、Cuとの複合添加により最適焼結温度領域を広げ、更に磁気特性中の特にiHcの増加に効果がある。0.02wt%未満ではiHcの増加の効果が非常に少なく、1.0wt%を超えるとBrの減少が大きくなるおそれがあるため、0.02~1.0wt%とすることがよい。

【0027】酸素含有量は、0.05wt%未満では過焼結になり易く角型性がよくなく、また0.5wt%を超えると酸化物の存在が本発明のZrB化合物、NbB化合物、HfB化合物を一緒に析出させる効果と同じ効果を発揮するため、0.05~0.5wt%とすることがよい。

【0028】炭素含有量は、0.03wt%未満では過焼結になり易く角型性がよくなく、また0.1wt%を超えると焼結性及び角型性が悪く、更には保磁力を減少させるおそれがあるため、0.03~0.1wt%とすることがよい。

【0029】窒素含有量は、0.002wt%未満では過焼結になり易く角型性がよくなく、また0.05wt%を超えると焼結性及び角型性が悪く、更には保磁力を減少させるおそれがあるため、0.002~0.05wt%とすることがよい。

【0030】本発明に用いるCuとZr, Nb又はHfは、原料として用いられるFeやAlとの合金や混合物でもよい。更に、使用原料中に含まれ、あるいは製造工程中に混入する0.2wt%以下の少量のLa, Ce, Sm, Ni, Mn, Si, Ca, Mg, S, P, W, Mo, Ta, Cr, Ga, Tiの存在は本発明の効果を損ねるものではない。

【0031】本発明の永久磁石材料は、後述する実施例に示すような所用の材料を用い、常法に従って合金を得た後、必要に応じて水素化処理、半脱水素処理を行い、微粉砕し、成型、焼結、熱処理することにより得ることができ、また二合金法を採用し、所望の組成にして用いることもできる。

【0032】本発明によれば、R-Fe-B-Cu系をベースとし、極く少量のZr, Nb又はHfを含むR-Fe-B-Cu-Zr, Nb又はHf系の一定の組成範囲において、合金鑄造、粉碎、成型、焼結、更に焼結温度よりも低い温度で熱処理することにより、残留磁束密度(Br)を少し増加させ、保磁力(iHc)を大幅に増加させ、角型性に優れ、更に最適焼結温度領域を20~60℃広げることができるものである。

【0033】従って、本発明の永久磁石材料は、その磁気特性がBrで12.5G以上、保磁力iHcが10kOe以上、角型比 $4 \times (BH)_{\max} / Br^2$ が0.95以上の優れた磁気特性を有するものとする事ができる。

【0034】

【実施例】以下、実施例及び比較例を示し、本発明を具体的に説明するが、本発明は下記の実施例に制限されるものではない。なお、下記の実施例、比較例の希土類永久磁石材料において、その $Fe_{14}R_2B_1$ 相の存在容量割合、希土類又は希土類と遷移金属の酸化物の存在容量割合、及び粒径100 μm 以上の $Fe_{14}R_2B_1$ 相の巨大異常成長粒の存在容量割合は、表13にまとめて示す。

【0035】【実施例1】出発原料として、Nd, Pr, Dy, 電解鉄, Co, フェロボロン, Al, Cu及びフェロジルコニウムを使用し、Zr添加の有無の比較として、重量比で27Nd-2Pr-1Dy-BAL, Fe-3Co-1B-0.5Al-0.2Cu-XZr (X=0, 0.2)の組成に配合後、双ロール急冷法により合金を得た。得られた合金を $+1.0 \pm 0.2 \text{ kgf/cm}^2$ の水素雰囲気中で水素化処理を行い、 10^{-2} Torr 以下の真空中で700°C×5時間の脱水素処理を行った。この時得られた合金は、水素化・脱水素処理によって数百 μm の粗粉になっている。得られた粗粉と潤滑剤として0.08wt%のオレイン酸をVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径3 μm 程度に微粉砕した。その後、これらの微粉を成型装置の金型に充填し、10kOeの磁界中で配向し、磁界に垂直方向に1.2ton/cm²の圧力で成型し、それらの成型体を1,020°Cから1,100°Cで2時間、Ar雰囲気中で焼結し、更に冷却した後、500°Cで1時間、Ar雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これらのR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.031~0.043、0.009~0.017、0.105~0.186wt%であった。

【0036】得られた磁気特性の結果を図1~3に示す。焼結温度と角型比の関係をを見ると、Zr無し品(比較例)は、1,020°Cと1,040°Cで焼結したものは角型比がそれぞれ0.954と0.955であり、良好であるが、Brを見ると1,020°Cは12.95kG、1,040°Cは13.24kGであり、1,020°C焼結品のBrは不十分な値である。このことから、Zr無し品の最適焼結温度は1,040°Cのみであることがわかる。一方、Zr添加品は1,040°Cと1,060°Cと1,080°CでBr、iHc、角型比が殆ど変化せずに良好であり、最適焼結温度幅が40°Cあることがわかる。更に、最適焼結温度では、Zr添加品の方がBrで100G、iHcで1kOe増加しており、Zrの添加が優れていることがわかる。

【0037】また、図4(a), (b)の焼結体の偏光像を見ると、Zr無し品(a)は約500 μm の異常粒成長部がこの領域で2カ所あることがわかる。

【0038】更に、EPMAによる元素分布像を見ると、Zr添加品は直径が5 μm 以下のZrB化合物が50 μm 以下の間隔で一様に細かく析出しており、また、EPMAによる定量分析の結果、このZrB化合物はZrとBが主成分であることがわかった。

【0039】これらのことから、Zrを添加し、焼結体中にZrB化合物を一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0040】【実施例2】出発原料として、Nd, Tb, 電解鉄, Co, フェロボロン, Al, Cu及びフェロジルコニウムを使用し、Zr添加の有無の比較として、重量比で30.0Nd-0.5Tb-BAL, Fe-1Co-1.1B-0.7Al-0.1Cu-XZr (X=0.01, 0.3, 1.2)の組成に配合後、高周波溶解し、水冷銅鑄型に鑄造することにより、各々の組成の鑄塊を得た。これらの鑄塊をブラウンミルで粗粉砕し、更に窒素気流中ジェットミルにて処理し、平均粒径3 μm 程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、15kOeの磁界中で配向し、磁界に垂直方向に0.7ton/cm²の圧力で成型し、その成型体を1,020°Cから1,100°Cで2時間、Ar雰囲気中で焼結し、更に冷却した後、600°Cで1時間、Ar雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これらのR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.081~0.092、0.003~0.01、0.058~0.081wt%であった。

【0041】得られた磁気特性の結果を図5~7に示す。焼結温度と角型比の関係をを見ると、Zr0.01品は、1,020°Cと1,040°Cで焼結したものは角型比がそれぞれ0.956と0.955であり、良好であるが、Brを見ると1,020°Cは13.07kG、1,040°Cは13.46kGであり、1,020°C焼結品のBrは劣化する傾向にある。一方、Zr0.3品は1,040°Cと1,060°Cと1,080°CでBr、iHc、角型比が殆ど変化せずに良好であり、最適焼結温度幅が40°Cあることがわかる。更に、Zr1.2品は1,040°Cと1,060°Cと1,080°CでBr、iHc、角型比が殆ど変化せず、最適焼結温度幅が40°Cあることがわかるが、Zr0.3品の方がBrで13.60~13.66kG、iHcで15.0~15.5kOeの磁気特性が得られており、Zr0.3品の添加の方が優れていることがわかる。

【0042】また、EPMAによる元素分布像を見ると、Zr0.3品は直径が5 μm 以下のZrB化合物が50 μm 以下の間隔で一様に細かく析出していた。一

方、Zr0.01品は直径が5 μ m以下のZrB化合物が50 μ m以上の間隔で析出しており、Zr0.3品と比べると若干一様さに欠けていた。更に、Zr1.2品は直径が5 μ m以下のZrB化合物が50 μ m以下の間隔で析出しているが、Zrの添加量が多すぎるため、磁気特性がZr0.3品と比べると劣化する傾向にあった。また、EPMAによる定量分析の結果、このZrB化合物はZrとBが主成分であることがわかった。

【0043】これらのことから、焼結体中に直径が5 μ m以下のZrB化合物を50 μ m以下の間隔で一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0044】[実施例3] 本発明を二合金法を利用することで更なる高特性化を試みた。以下の4つの実施例3-1、実施例3-2、実施例3-3、実施例3-4においては、実験条件は母合金と助材の組成のみを変化させてあり、母合金は単ロール急冷法により作製し、+0.5~+2.0kgf/cm²の水素雰囲気中で水素化処理を行い、10⁻²Torr以下の真空中で500℃×3時間の半脱水素処理を行った。また、助材合金は高周波溶解し、水冷銅鑄型に鑄造することにより鑄塊を得た。

【0045】次に、母合金を90wt%と助材を10wt%秤量し、潤滑剤としてステアリン酸亜鉛を0.05wt%添加してVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径4 μ m程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、12kOeの磁界中で配向し、磁界に垂直方向に0.5ton/cm²の圧力で成型し、その成型体を1,020℃から10℃毎に1,100℃まで2時間、10⁻⁴Torr以下の真空雰囲気中で焼結し、更に冷却した後、500℃で1時間、10⁻²Torr以下の真空雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。

【0046】実施例3-1

母合金は重量比で30.0Nd-BAL. Fe-4.6Co-1.4B-0.2Al-XZr (X=0, 0.5)の組成に、助材合金は重量比で36.0Nd-10.2Dy-BAL. Fe-25.8Co-0.2Al-2.4Cuの組成にした。混合後の組成は29.7Nd-1.0Dy-BAL. Fe-6.7Co-1.2B-0.2Al-0.24Cu-XZr (X=0, 0.4

5)である。

【0047】実施例3-2

母合金は重量比で28.4Nd-BAL. Fe-1.9Co-1.3B-0.4Al-XZr (X=0, 0.4)の組成に、助材合金は重量比で36.9Nd-10.2Tb-BAL. Fe-30.2Co-0.6B-0.3Al-3.2Cuの組成にした。混合後の組成は29.3Nd-1.0Tb-BAL. Fe-4.7Co-1.2B-0.4Al-0.32Cu-XZr (X=0, 0.39)である。

【0048】実施例3-3

母合金は重量比で27.2Nd-BAL. Fe-0.9Co-1.0B-0.2Alの組成に、助材合金は重量比で50.1Nd-9.4Dy-BAL. Fe-23.9Co-1.0B-0.2Al-1.1Cu-XZr (X=0, 1.1)の組成にした。混合後の組成は29.5Nd-0.9Dy-BAL. Fe-3.2Co-1.0B-0.2Al-0.1Cu-XZr (X=0, 0.11)である。

【0049】実施例3-4

母合金は重量比で27.0Nd-1.0Dy-BAL. Fe-4.6Co-1.3B-0.4Al-XZr (X=0, 0.45)の組成に、助材合金は重量比で35.5Nd-9.8Tb-BAL. Fe-29.0Co-0.3Al-2.3Cu-XZr (X=0, 0.45)の組成にした。混合は、Zrなし母合金とZrなし助材、及びZrあり母合金とZrあり助材をそれぞれ混合した。混合後の組成は27.9Nd-2.3Dy-1.0Tb-BAL. Fe-7.0Co-1.1B-0.4Al-0.2Cu-XZr (X=0, 0.45)である。

【0050】得られた結果を表1~4に示す。表1~4より実施例3-1、実施例3-2、実施例3-3、実施例3-4のいずれの場合でも、Zrを添加したものはBr、iHc、角型比が無添加のものよりも優れており、更に最適焼結温度領域もZrを添加することにより拡大していることがわかる。

【0051】

【表1】

実施例 3-1

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,060℃のみ	13.63	12.8	0.968
0.45	1,060~1,070℃	13.64~13.61	13.2~13.8	0.963~0.966

【0052】

【表2】

実施例 3-2

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,080℃のみ	13.46	12.5	0.967
0.39	1,060~1,080℃	13.63~13.61	13.3~13.8	0.959~0.964

【0053】

【表3】

実施例 3.3

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,060℃のみ	13.58	13.1	0.956
0.11	1,060～1,080℃	13.61～13.66	13.7～14.1	0.961～0.963

【0054】

【表4】

実施例 3.4

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,080℃のみ	12.88	16.9	0.956
0.45	1,080～1,100℃	12.92～13.02	17.1～17.7	0.961～0.963

【0055】更に、EPMAによる元素分布像を見ると、実施例3-1、実施例3-2、実施例3-3、実施例3-4のいずれの場合でも、Zr添加品は直径が5 μ m以下のZrB化合物が50 μ m以下の間隔で一様に細かく析出していた。また、EPMAによる定量分析の結果、このZrB化合物はZrとBが主成分であることがわかった。

【0056】これらのことから、二合金法においてもZrを添加し、焼結体中にZrB化合物を一様に細かく析出させることによって異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0057】[実施例4] 出発原料として、Nd, Pr, Dy, 電解鉄, Co, フェロボロン, Al, Cu及びフェロニウムを使用し、Nb添加の有無の比較として、重量比で26.5Nd-2.2Pr-2.5Dy-BAL, Fe-4.5Co-1.1B-0.4Al-0.5Cu-XNb (X=0, 0.2)の組成に配合後、双ロール急冷法により合金を得た。得られた合金を+1.5 \pm 0.3kgf/cm²の水素雰囲気中で水素化処理を行い、10⁻²Torr以下の真空中で800℃ \times 5時間の脱水素処理を行った。この時得られた合金は、水素化・脱水素処理によって数百 μ mの粗粉になっている。得られた粗粉と潤滑剤として0.05wt%のステアリン酸亜鉛をVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径3 μ m程度に微粉碎した。その後、これらの微粉を成型装置の金型に充填し、15kOeの磁界中で配向し、磁界に垂直方向に0.5ton/cm²の圧力で成型し、それらの成型体を1,000℃から1,080℃で2時間、Ar雰囲気中で焼結し、更に冷却した後、500℃で1時間、Ar雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これらのR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.061～0.073、0.019～0.027、0.095～0.116wt%であった。

【0058】得られた磁気特性の結果を図8～10に示す。焼結温度と角型比の関係をみると、Nb無し品は、1,000℃と1,020℃で焼結したものは角型比がそれぞれ0.951と0.955であり、良好であるが、Brを見ると1,000℃は12.87kG、1,020℃は13.23kGであり、1,000℃焼結品

のBrは不十分な値である。このことから、Nb無し品の最適焼結温度は1,020℃のみであることがわかる。一方、Nb添加品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せずに良好であり、最適焼結温度幅が40℃あることがわかる。更に、最適焼結温度では、Nb添加品の方がBrで80G、iHcで500Oe増加しており、Nbの添加が優れていることがわかる。

【0059】また、焼結体の偏光像によると、Nb無し品(a)は約500 μ mの異常粒成長部がこの領域で2カ所あることがわかった。

【0060】更に、EPMAによる元素分布像を見ると、Nb添加品は直径が5 μ m以下のNbB化合物が50 μ m以下の間隔で一様に細かく析出していた。また、EPMAによる定量分析の結果、このNbB化合物はNbとBが主成分であることがわかった。

【0061】これらのことから、Nbを添加し、焼結体中にNbB化合物を一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0062】[実施例5] 出発原料として、Nd, Tb, 電解鉄, Co, フェロボロン, Al, Cu及びフェロニウムを使用し、Nb添加量の検討として、重量比で29.1Nd-0.2Tb-BAL, Fe-2.7Co-1.2B-0.4Al-0.5Cu-XNb (X=0.01, 0.57, 1.15)の組成に配合後、高周波溶解し、水冷銅鑄型に鑄造することにより、各々の組成の鑄塊を得た。これらの鑄塊をブラウンミルで粗粉碎し、更に窒素気流中ジェットミルにて処理し、平均粒径5 μ m程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、12kOeの磁界中で配向し、磁界に垂直方向に1.2ton/cm²の圧力で成型し、その成型体を1,000℃から1,080℃で2時間、10⁻⁴Torr以下の真空雰囲気中で焼結し、更に冷却した後、500℃で1時間、10⁻²Torr以下の真空雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これらのR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.030～0.038、0.027～0.041、0.328～0.418wt%であった。

【0063】得られた磁気特性の結果を図11～13に

示す。焼結温度と角型比の関係をみると、Nb_{0.01}品は、1,000℃と1,020℃で焼結したものは角型比がそれぞれ0.951と0.953であり、良好であるが、Brを見ると1,000℃は13.37kG、1,020℃は13.55kGであり、1,000℃焼結品のBrは劣化する傾向にある。一方、Nb_{0.57}品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せずに良好であり、最適焼結温度幅が40℃あることがわかる。更に、Nb_{1.15}品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せず、最適焼結温度幅が40℃あることがわかるが、Nb_{0.57}品の方がBrで13.65~13.67kG、iHcで14.9~15.2kOeの磁気特性が得られており、Nb_{0.57}品の添加の方が優れていることがわかる。

【0064】また、EPMAによる元素分布像を見ると、Nb_{0.57}品は直径が5μm以下のNbB化合物が50μm以下の間隔で一様に細かく析出していた。更に、Nb_{1.15}品は直径が5μm以下のNbB化合物が50μm以下の間隔で析出していたが、Nbの添加量が多すぎるため、磁気特性がNb_{0.57}品と比べると低い傾向にあった。また、EPMAによる定量分析の結果、このNbB化合物はNbとBが主成分であることがわかった。

【0065】これらのことから、焼結体中に直径が5μm以下のNbB化合物を50μm以下の間隔で一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0066】〔実施例6〕本発明を二合金法を利用することで更なる高特性化を試みた。以下の4つの実施例6-1、実施例6-2、実施例6-3、実施例6-4においては、実験条件は母合金と助材の組成のみを変化させてあり、母合金は単ロール急冷法により作製し、+0.5~+2.0kgf/cm²の水素雰囲気中で水素化処理を行い、10⁻²Torr以下の真空中で500℃×3時間の半脱水素処理を行った。また、助材合金は高周波溶解し、水冷銅鑄型に鑄造することにより鑄塊を得た。

【0067】次に、母合金を92wt%と助材を8wt%秤量し、潤滑剤としてステアリン酸亜鉛を0.05wt%添加してVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径4μm程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、12kOeの磁界中で配向し、磁界に垂直方向に0.5ton/cm²の圧力で成型し、その成型体を1,020℃から10℃毎に1,100℃まで2時間、10⁻⁴Torr以下の真空雰囲気中で焼結し、更に冷却した後、500℃で1時間、10⁻²Torr以下のArガス雰囲気中で

熱処理し、各々の組成の永久磁石材料を得た。

【0068】実施例6-1

母合金は重量比で27.9Nd-BAL、Fe-7.3Co-1.3B-0.2Al-XNb (X=0, 0.4)の組成に、助材合金は重量比で36.0Nd-10.2Dy-BAL、Fe-25.8Co-0.2Al-2.4Cuの組成にした。混合後の組成は28.6Nd-3.1Dy-BAL、Fe-8.8Co-1.2B-0.2Al-0.2Cu-XNb (X=0, 0.4)である。

【0069】実施例6-2

母合金は重量比で28.1Nd-1.2Tb-BAL、Fe-3.7Co-1.2B-0.4Al-XNb (X=0, 0.7)の組成に、助材合金は重量比で36.9Nd-10.2Tb-BAL、Fe-30.2Co-0.6B-0.3Al-3Cuの組成にした。混合後の組成は28.8Nd-2.0Tb-BAL、Fe-5.8Co-1.1B-0.4Al-0.3Cu-XNb (X=0, 0.7)である。

【0070】実施例6-3

母合金は重量比で27.2Nd-BAL、Fe-0.9Co-1.0B-0.2Alの組成に、助材合金は重量比で47.2Nd-8.9Dy-8.7Tb-BAL、Fe-22.5Co-0.1Al-1.4Cu-XNb (X=0, 1.0)の組成にした。混合後の組成は28.8Nd-0.7Dy-0.7Tb-BAL、Fe-2.7Co-1.0B-0.2Al-0.1Cu-XNb (X=0, 0.1)である。

【0071】実施例6-4

母合金は重量比で27.0Nd-2.5Dy-BAL、Fe-4.6Co-1.3B-0.4Al-XNb (X=0, 0.4)の組成に、助材合金は重量比で35.5Nd-9.8Tb-BAL、Fe-29.0Co-0.3Al-2.3Cu-XNb (X=0, 0.4)の組成にした。混合は、Nbなし母合金とNbなし助材、及びNbあり母合金とNbあり助材をそれぞれ混合した。混合後の組成は27.7Nd-2.3Dy-0.8Tb-BAL、Fe-6.6Co-1.2B-0.4Al-0.2Cu-XNb (X=0, 0.4)である。

【0072】得られた結果を表5~8に示す。表5~8より実施例6-1、実施例6-2、実施例6-3、実施例6-4のいずれの場合でも、Nbを添加したものはBr、iHc、角型比が無添加のものよりも優れており、更に最適焼結温度領域もNbを添加することにより拡大していることがわかる。

【0073】

【表5】

実施例 6-1

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,040℃のみ	13.24	16.8	0.952
0.4	1,040～1,080℃	13.28～13.33	16.6～16.8	0.961～0.966

【0074】

【表6】

実施例 6-2

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.46	16.6	0.954
0.7	1,030～1,070℃	13.54～13.61	16.3～16.8	0.965～0.969

【0075】

【表7】

実施例 6-3

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.58	16.1	0.961
0.1	1,030～1,070℃	13.61～13.66	16.9～16.6	0.961～0.967

【0076】

【表8】

実施例 6-4

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,040℃のみ	13.66	14.8	0.969
0.4	1,040～1,080℃	13.66～13.72	15.5～16.1	0.967～0.970

【0077】更に、EPMAによる元素分布像を見ると、実施例6-1、実施例6-2、実施例6-3、実施例6-4のいずれの場合でも、Nb添加品は直径が5 μ m以下のNbB化合物が50 μ m以下の間隔で一様に細かく析出していた。また、EPMAによる定量分析の結果、このNbB化合物はNbとBが主成分であることがわかった。

【0078】これらのことから、二合金法においてもNbを添加し、焼結体中にNbB化合物を一様に細かく析出させることによって異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0079】[実施例7] 出発原料として、Nd、Pr、Tb、電解鉄、Co、フェロボロン、Al、Cu及びフェロハフニウムを使用し、Hf添加の有無の比較として、重量比で28.5Nd-1.0Pr-0.5Tb-BAL、Fe-4.0Co-1.3B-0.4Al-0.5Cu-XHf (X=0, 0.4)の組成に配合後、双ロール急冷法により合金を得た。得られた合金を+2.0 \pm 0.5kgf/cm²の水素雰囲気中で水素化処理を行い、10⁻²Torr以下の真空中で400℃ \times 3時間の脱水素処理を行った。この時得られた合金は、水素化・脱水素処理によって数百 μ mの粗粉になっている。得られた粗粉と潤滑剤として0.05wt%のサフィノールをVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径5 μ m程度に微粉砕した。その後、これらの微粉を成型装置の金型に充填し、12kOeの磁界中で配向し、磁界に垂直方向に1.0ton/cm²の圧力で成型し、それらの成型体を1,000℃から1,080℃で2時間、Ar雰囲気中で焼結し、更に冷却した後、500℃で1時間、Ar雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これら

のR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.051～0.063、0.029～0.037、0.135～0.216wt%であった。

【0080】得られた磁気特性の結果を図14～16に示す。焼結温度と角型比の関係をみると、Hf無し品は、1,000℃と1,020℃で焼結したものは角型比がそれぞれ0.951と0.955であり、良好であるが、Brを見ると1,000℃は12.93kG、1,020℃は13.43kGであり、1,000℃焼結品のBrは不十分な値である。このことから、Hf無し品の最適焼結温度は1,020℃のみであることがわかる。一方、Hf添加品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せず良好であり、最適焼結温度幅が40℃あることがわかる。更に、最適焼結温度では、Hf添加品の方がBrで80G、iHcで700Oe増加しており、Hfの添加が優れていることがわかる。

【0081】また、焼結体の偏光像を見ると、Hf無し品(a)は約500 μ mの異常粒成長部がこの領域で2カ所あることがわかった。

【0082】更に、EPMAによる元素分布像を見ると、Hf添加品は直径が5 μ m以下のHfB化合物が50 μ m以下の間隔で一様に細かく析出していた。また、EPMAによる定量分析の結果、このHfB化合物はHfとBが主成分であることがわかった。

【0083】これらのことから、Hfを添加し、焼結体中にHfB化合物を一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0084】[実施例8] 出発原料として、Nd、P

r, Dy, 電解鉄, Co, フェロボロン, Al, Cu及びフェロハフニウムを使用し、Hf添加量の検討として、重量比で28.7Nd-2.2Pr-1.2Dy-BAL. Fe-3.6Co-1.2B-0.4Al-0.5Cu-XHf (X=0.01, 0.41, 1.22)の組成に配合後、高周波溶解し、水冷銅鑄型に鑄造することにより、各々の組成の鑄塊を得た。これらの鑄塊をブラウンミルで粗粉碎し、更に窒素気流中ジェットミルにて処理し、平均粒径5 μ m程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、15kOeの磁界中で配向し、磁界に垂直方向に0.7ton/cm²の圧力で成型し、その成型体を1,000℃から1,080℃で2時間、Ar雰囲気中で焼結し、更に冷却した後、600℃で1時間、Ar雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。なお、これらのR-Fe-B系永久磁石材料における炭素、窒素、酸素含有量は、それぞれ0.031~0.041、0.023~0.040、0.228~0.411wt%であった。

【0085】得られた磁気特性の結果を図17~19に示す。焼結温度と角型比の関係をみると、Hf0.01品は、1,000℃と1,020℃で焼結したものは角型比がそれぞれ0.951と0.953であり、良好であるが、Brを見ると1,000℃は12.93kG、1,020℃は13.35kGであり、1,000℃焼結品のBrは劣化する傾向にある。一方、Hf0.41品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せずに良好であり、最適焼結温度幅が40℃あることがわかる。更に、Hf1.22品は1,020℃と1,040℃と1,060℃でBr、iHc、角型比が殆ど変化せず、最適焼結温度幅が40℃あることがわかるが、Hf0.41品の方がBrで13.45~13.47kG、iHcで13.2~13.5kOeの磁気特性が得られており、Hf0.41品の添加の方が優れていることがわかる。

【0086】また、EPMAによる元素分布像を見ると、Hf0.41品は直径が5 μ m以下のHfB化合物が50 μ m以下の間隔で一様に細かく析出していた。更に、Hf1.22品は直径が5 μ m以下のHfB化合物が50 μ m以下の間隔で析出していたが、Hfの添加量が多すぎるため、磁気特性がHf0.41品と比べると低いことがわかった。また、EPMAによる定量分析の結果、このHfB化合物はHfとBが主成分であることがわかった。

【0087】これらのことから、焼結体中に直径が5 μ m以下のHfB化合物を50 μ m以下の間隔で一様に細かく析出させることによって、異常粒成長を抑制し、最適焼結温度幅を広げていることがわかる。

【0088】[実施例9]本発明を二合金法を利用することで更なる高特性化を試みた。以下の4つの実施例9

-1、実施例9-2、実施例9-3、実施例9-4においては、実験条件は母合金と助材の組成のみを変化させてあり、母合金は単ロール急冷法により作製し、+0.5~+2.0kgf/cm²の水素雰囲気中で水素化処理を行い、10⁻²Torr以下の真空中で500℃×3時間の半脱水素処理を行った。また、助材合金は高周波溶解し、水冷銅鑄型に鑄造することにより鑄塊を得た。

【0089】次に、母合金を88wt%と助材を12wt%秤量し、潤滑剤としてステアリン酸亜鉛を0.05wt%添加してVミキサーで混合し、更に窒素気流中ジェットミルにて平均粒径4 μ m程度の微粉を得た。その後、これらの微粉を成型装置の金型に充填し、12kOeの磁界中で配向し、磁界に垂直方向に0.5ton/cm²の圧力で成型し、その成型体を1,020℃から10℃毎に1,100℃まで2時間、10⁻⁴Torr以下の真空雰囲気中で焼結し、更に冷却した後、500℃で1時間、10⁻²Torr以下の真空雰囲気中で熱処理し、各々の組成の永久磁石材料を得た。

【0090】実施例9-1

母合金は重量比で27.2Nd-BAL. Fe-0.9Co-1.0B-0.2Alの組成に、助材合金は重量比で49.6Nd-9.3Dy-BAL. Fe-23.6Co-0.2Al-1.1Cu-XHf (X=0.02)の組成にした。混合後の組成は29.9Nd-1.1Dy-BAL. Fe-3.7Co-1.0B-0.2Al-0.1Cu-XHf (X=0.02)である。

【0091】実施例9-2

母合金は重量比で28.0Nd-2.5Dy-BAL. Fe-4.6Co-1.3B-0.4Alの組成に、助材合金は重量比で34.0Nd-9.4Tb-BAL. Fe-27.8Co-0.3Al-2.2Cu-XHf (X=0.84)の組成にした。混合後の組成は28.7Nd-2.2Dy-1.1Tb-BAL. Fe-7.4Co-1.1B-0.4Al-0.3Cu-XHf (X=0.10)である。

【0092】実施例9-3

母合金は重量比で28.0Nd-1.3Dy-BAL. Fe-7.3Co-1.3B-0.2Al-0.5Cu-XHf (X=0.07)の組成に、助材合金は重量比で36.0Nd-10.2Dy-BAL. Fe-25.8Co-0.2Al-2.4Cuの組成にした。混合後の組成は29.0Nd-2.3Dy-BAL. Fe-9.5Co-1.2B-0.2Al-0.7Cu-XHf (X=0.07)である。

【0093】実施例9-4

母合金は重量比で27.0Nd-1.2Tb-BAL. Fe-3.7Co-1.2B-0.4Al-0.3Cu-XHf (X=0.07)の組成に、助材合金は重量比で36.9Nd-10.2Tb-BAL. Fe-3

0.2Co-0.3Al-3.3Cu-0.7Hfの組成にした。混合後の組成は28.2Nd-2.3Tb-BAL. Fe-6.9Co-1.1B-0.4Al-0.7Cu-XHf (X=0, 0.7)である。

【0094】得られた結果を表9～12に示す。表9～12より実施例9-1、実施例9-2、実施例9-3、

実施例9-4のいずれの場合でも、Hfを添加したものはBr、iHc、角型比が無添加のものよりも優れており、更に最適焼結温度領域もHfを添加することにより拡大していることがわかる。

【0095】

【表9】

実施例 9-1

Hf量	最適焼結温度領域	Br	iHc	角型比
0	1,020℃のみ	13.43	14.8	0.955
0.2	1,020～1,060℃	13.48～13.59	15.2～15.8	0.961～0.965

【0096】

【表10】

実施例 9-2

Hf量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	12.85	17.5	0.952
1.0	1,030～1,070℃	12.91～13.01	18.3～18.8	0.962～0.964

【0097】

【表11】

実施例 9-3

Hf量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.18	16.1	0.956
0.7	1,030～1,070℃	13.31～13.36	16.7～17.1	0.964～0.968

【0098】

【表12】

実施例 9-4

Hf量	最適焼結温度領域	Br	iHc	角型比
0	1,020℃のみ	13.16	16.8	0.951
0.7	1,020～1,060℃	13.25～13.32	17.5～18.1	0.966～0.969

【0099】更に、EPMAによる元素分布像を見ると、実施例9-1、実施例9-2、実施例9-3、実施例9-4のいずれの場合でも、Hf添加品は直径が5μm以下のHfB化合物が50μm以下の間隔で一様に細かく析出していた。また、EPMAによる定量分析の結果、このHfB化合物はHfとBが主成分であることがわかった。

【0100】これらのことから、二合金法においてもHfを添加し、焼結体中にHfB化合物を一様に細かく析出させることによって異常粒成長を抑制し、最適焼結温

度幅を広げていることがわかる。

【0101】なお、助材合金を高周波溶解し、水冷鋳型に鋳造し、水素化・半脱水素処理することや、助材合金を単又は双ロール急冷法により作製し、水素化・半脱水素処理することや、助材合金を単又は双ロール急冷法により作製し、ブラウンミル等で粗粉砕する方法も本発明には有効である。

【0102】

【表13】

		Fe ₁₄ R ₂ B ₁ (%)	酸化物 (%)	異常成長粒 (%)
実施例 1	Zr 0(比較例)	93.2	2.2	3.9
	Zr 0.2	93.1	2.1	0.5
実施例 2	Zr 0.01	94.1	0.9	4.0
	Zr 0.3	94.2	0.8	1.3
	Zr 1.2	93.7	1.0	1.4
実施例 3-1	Zr 0(比較例)	95.0	1.1	4.1
	Zr 0.45	95.0	1.0	0.5
実施例 3-2	Zr 0(比較例)	94.3	0.6	5.2
	Zr 0.39	94.4	0.5	1.3
実施例 3-3	Zr 0(比較例)	96.8	2.0	3.5
	Zr 0.11	96.7	2.1	0.8
実施例 3-4	Zr 0(比較例)	89.1	0.2	3.9
	Zr 0.45	89.2	0.1	2.0
実施例 4	Nb 0(比較例)	94.2	1.2	4.9
	Nb 0.2	94.1	1.1	0.8
実施例 5	Nb 0.01	91.1	1.9	5.0
	Nb 0.57	91.2	1.8	1.7
	Nb 1.15	90.2	2.0	1.7
実施例 6-1	Nb 0(比較例)	92.0	2.1	4.5
	Nb 0.4	92.1	2.0	0.9
実施例 6-2	Nb 0(比較例)	94.7	0.4	5.1
	Nb 0.7	94.6	0.3	1.0
実施例 6-3	Nb 0(比較例)	95.8	1.0	3.8
	Nb 0.1	95.7	1.1	1.8
実施例 6-4	Nb 0(比較例)	88.1	1.2	3.5
	Nb 0.4	88.2	1.1	1.0
実施例 7	Hf 0(比較例)	91.2	2.2	4.9
	Hf 0.4	91.1	2.1	0.7
実施例 8	Hf 0.01	94.8	1.9	5.0
	Hf 0.41	94.9	1.8	0.3
	Hf 1.22	94.0	2.0	0.4
実施例 9-1	Hf 0(比較例)	88.0	1.6	5.1
	Hf 0.2	88.0	1.7	1.5
実施例 9-2	Hf 0(比較例)	91.3	2.6	4.2
	Hf 1.0	91.4	2.5	1.1
実施例 9-3	Hf 0(比較例)	96.8	1.0	3.7
	Hf 0.7	96.9	1.1	0.5
実施例 9-4	Hf 0(比較例)	90.1	0.3	3.3
	Hf 0.7	90.0	0.4	1.0

【0103】

【発明の効果】本発明によれば、高特性のR-Fe-B系希土類永久磁石材料を得ることができる。

【図面の簡単な説明】

【図1】実施例1におけるZr無し品とZr有り品の焼結温度と角型比との関係を示すグラフである。

【図2】実施例1におけるZr無し品とZr有り品の焼結温度とiHcとの関係を示すグラフである。

【図3】実施例1におけるZr無し品とZr有り品の焼結温度とBrとの関係を示すグラフである。

【図4】実施例1におけるZr無し品(a)とZr有り品(b)の偏光像である。

【図5】実施例2における異なるZr量の合金の焼結温度と角型比との関係を示すグラフである。

【図6】実施例2における異なるZr量の合金の焼結温度とiHcとの関係を示すグラフである。

【図7】実施例2における異なるZr量の合金の焼結温度とBrとの関係を示すグラフである。

【図8】実施例4におけるNb無し品とNb有り品の焼結温度と角型比との関係を示すグラフである。

【図9】実施例4におけるNb無し品とNb有り品の焼

結温度とiHcとの関係を示すグラフである。

【図10】実施例4におけるNb無し品とNb有り品の焼結温度とBrとの関係を示すグラフである。

【図11】実施例5における異なるNb量の合金の焼結温度と角型比との関係を示すグラフである。

【図12】実施例5における異なるNb量の合金の焼結温度とiHcとの関係を示すグラフである。

【図13】実施例5における異なるNb量の合金の焼結温度とBrとの関係を示すグラフである。

【図14】実施例7におけるHf無し品とHf有り品の焼結温度と角型比との関係を示すグラフである。

【図15】実施例7におけるHf無し品とHf有り品の焼結温度とiHcとの関係を示すグラフである。

【図16】実施例7におけるHf無し品とHf有り品の焼結温度とBrとの関係を示すグラフである。

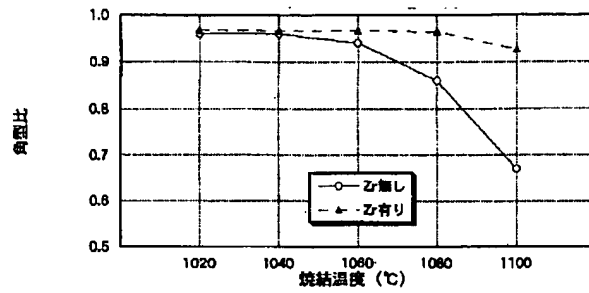
【図17】実施例8における異なるHf量の合金の焼結温度と角型比との関係を示すグラフである。

【図18】実施例8における異なるHf量の合金の焼結温度とiHcとの関係を示すグラフである。

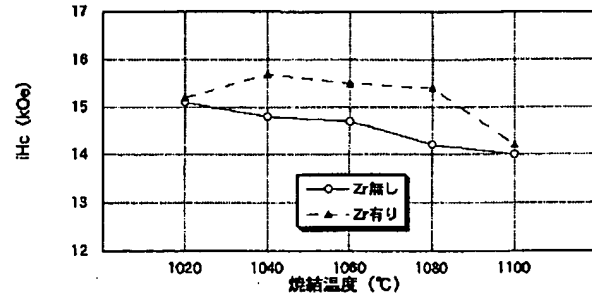
【図19】実施例8における異なるHf量の合金の焼結温度とBrとの関係を示すグラフである。

【図20】(a), (b)はそれぞれ従来例における巨大異常成長粒を示す顕微鏡写真である。

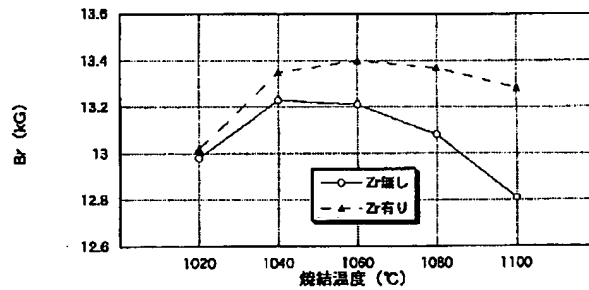
【図1】



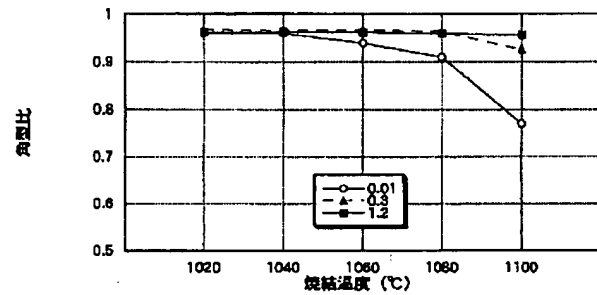
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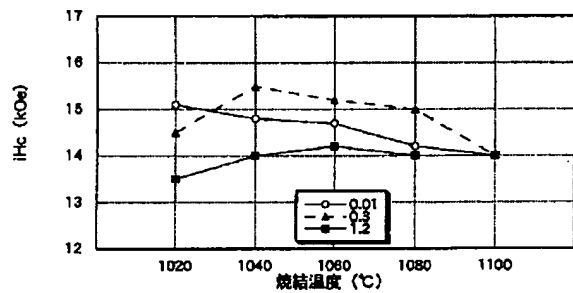
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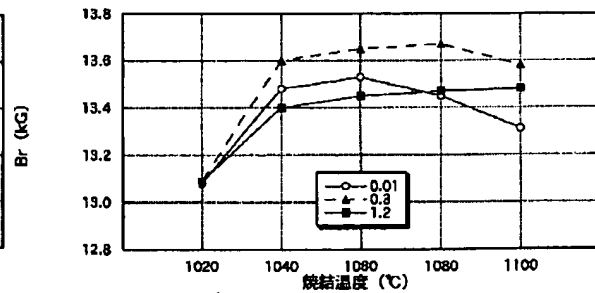
【図5】



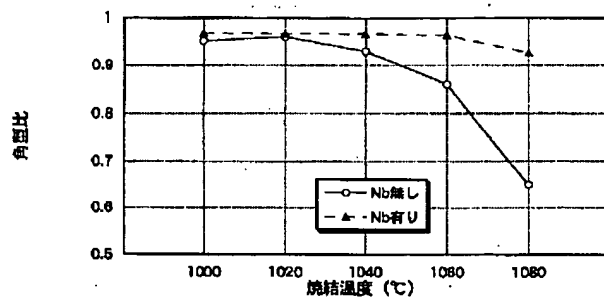
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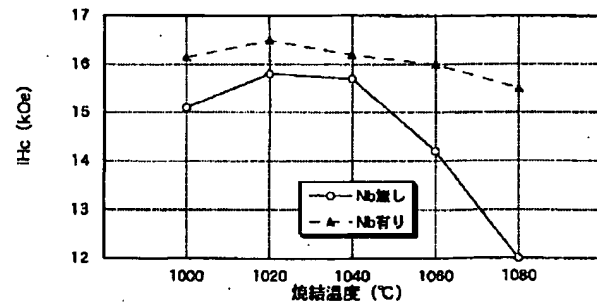
【図7】



【図8】

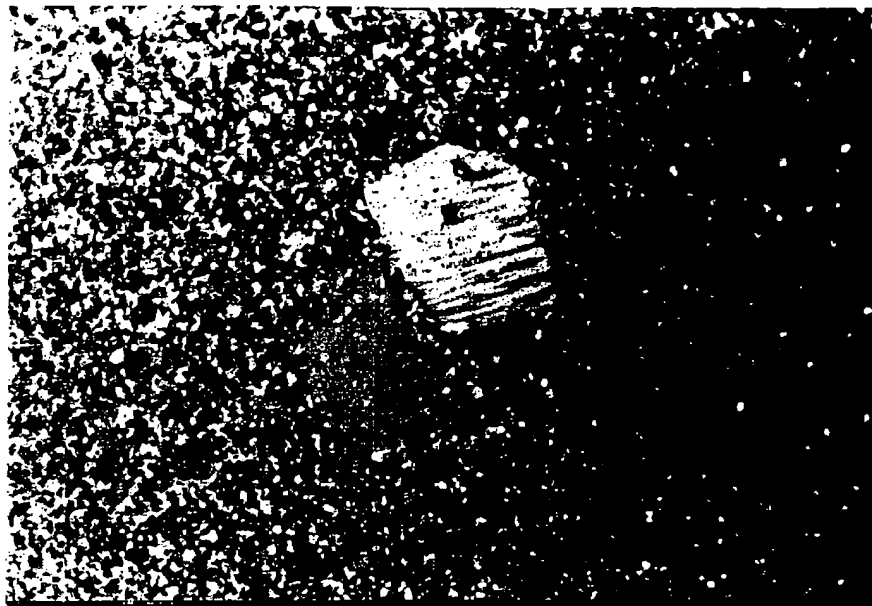


【図9】

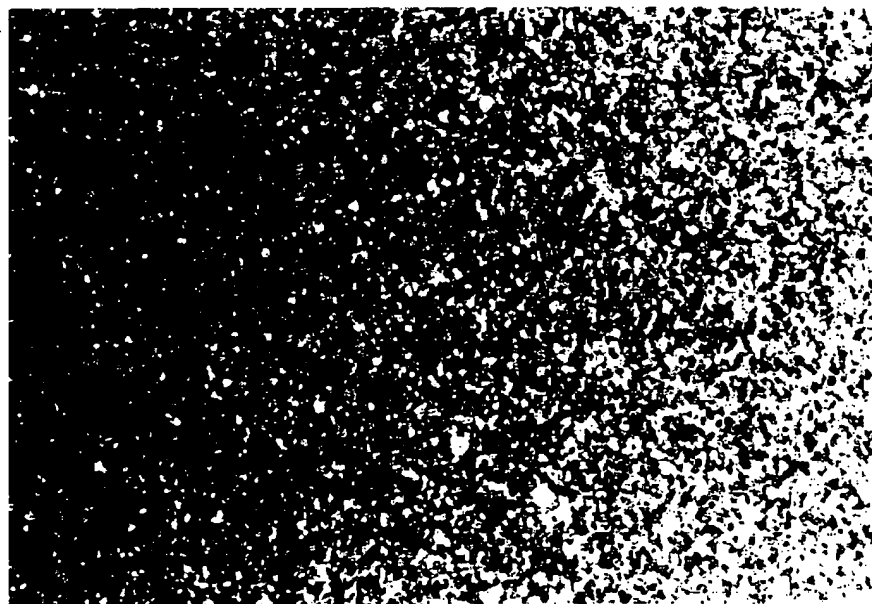


【図4】

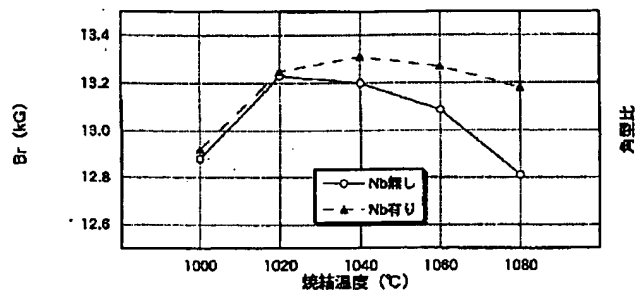
(a)



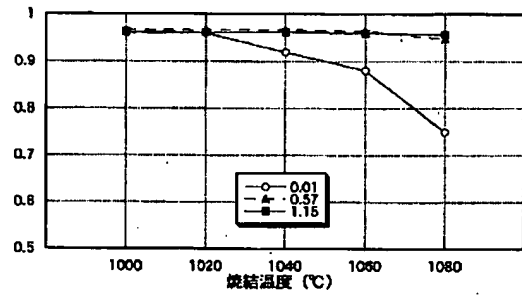
(b)



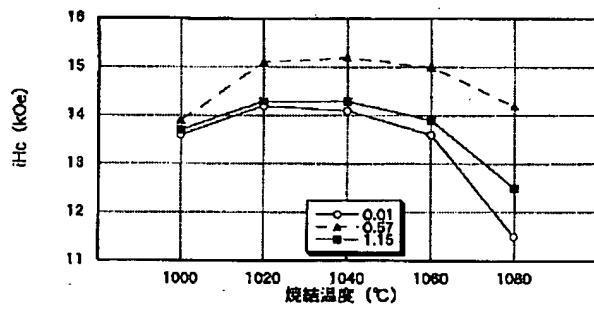
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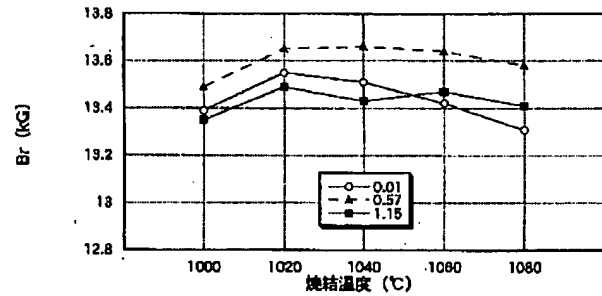
【図11】



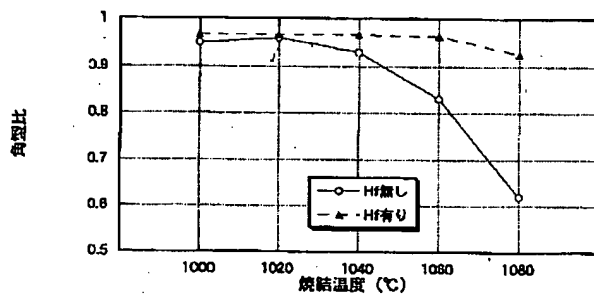
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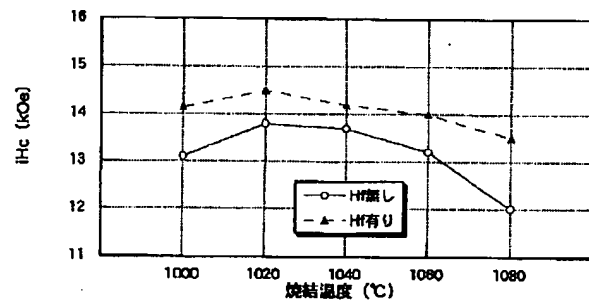
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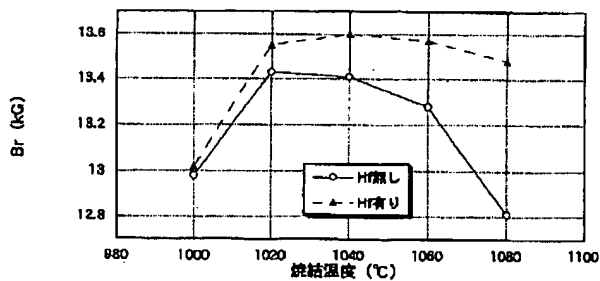
【図14】



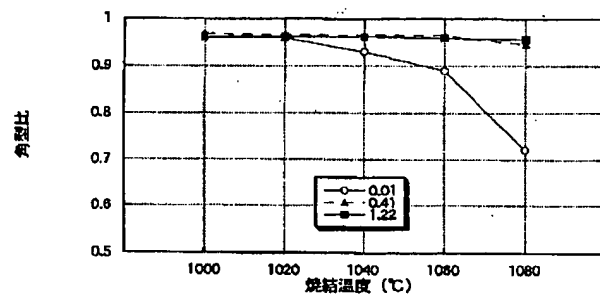
【図15】



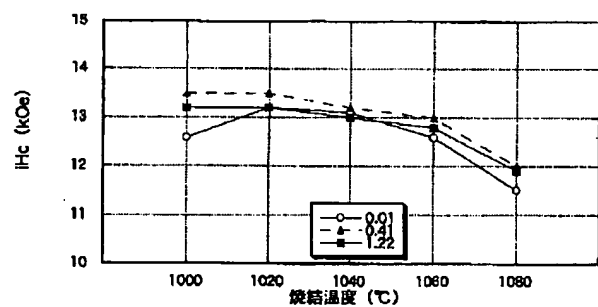
【図16】



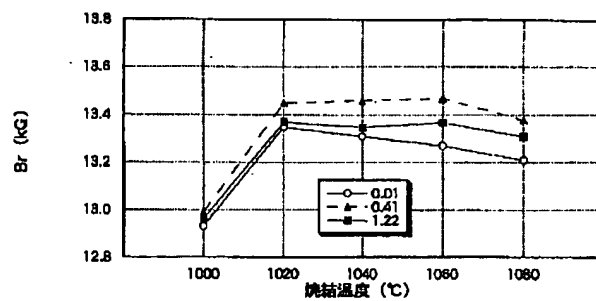
【図17】



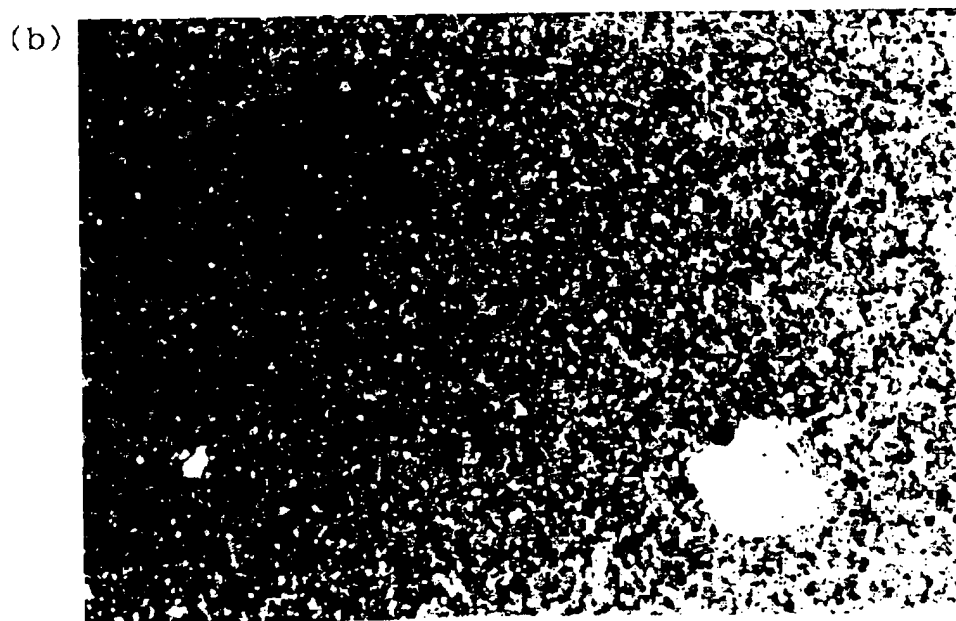
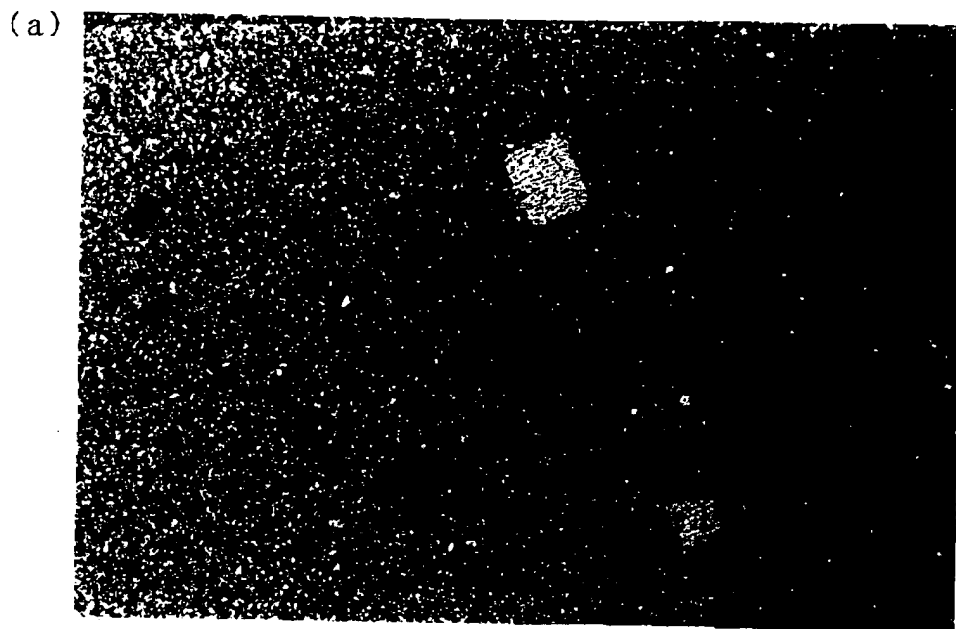
【図18】



【図19】



【図20】



フロントページの続き

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(54) R-Fe-B RARE EARTH PERMANENT MAGNET MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an R-Fe-B rare earth permanent magnet material, in which abnormal grains are grown less, even if an alloy is decreased in oxygen content by separating out ZrB compound, NbB compound, or HfB compound finely and uniformly in a magnet, so as to markedly expand its range of optimal sintering temperature.

SOLUTION: An RFeB magnet alloy is composed of 87.5 to 97.5 vol.%

Fe₁₄R₂B₁ phase (wherein, R denotes at least a kind of rare earth element) and 0.1 to 3 vol.% rare earth or rare earth and oxide of transition metal. A compound selected out of a ZrB compound composed of Zr and B, an NbB compound composed of Nb and B, or an HfB compound composed of Hf and B as main components is contained in the metallic structure of the above alloy, and the compound grains are smaller than 5 μm in average grain diameter and dispersed in the alloy at a maximum interval of 50 μm or smaller.

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CLAIMS

[Claim(s)]

[Claim 1] The Fe₁₄R₂B plane's 1 (however, R's shows at least one sort of rare earth elements') which is main phase component's existence capacity percentage is 87.5 - 97.5%. In the RFeB system magnet alloy whose oxide's of rare earth or rare earth, and transition metals existence capacity percentage is 0.1 - 3% The compound chosen from the ZrB compound which consists of Zr and B as a principal component all over the metal texture of this alloy, the NbB compound which consists of Nb and B, and the HfB compound which consists of Hf and B with the mean particle diameter of 5 micrometers or less And the R-Fe-B system rare earth permanent magnet ingredient characterized by the maximum spacing between the ZrB compound which adjoins each other and exists in the above-mentioned alloy, a NbB compound, and the compound chosen from a HfB compound distributing to homogeneity by 50 micrometers or less.

[Claim 2] The permanent magnet ingredient according to claim 1 whose huge abnormality growth grain of a Fe₁₄R₂B plane 1 with a particle size of 100 micrometers or more is 3% or less at an existence capacity rate to the whole metal texture.

[Claim 3] The permanent magnet ingredient according to claim 1 or 2 10 or more kOes and whose square shape ratio $4 \times (BH)_{\max} / Br^2$ more than 12.5G and coercive force iH_c are 0.95 or more in Br for magnetic properties.

[Claim 4] A RFeB system magnet alloy is R_{27-33%} (however, although R shows

one sort of rare earth elements, or two sorts or more) at weight percent. 0.1 - 10% [of Co(es) which contain Nd 15 to 33%] B 0.9 - 1.5%, 0.02 - 1.0% of elements chosen from 0.05 - 1.0% of aluminum, 0.02 - 1.0% of Cu(s), and Zr, Nb and Hf, The permanent magnet ingredient according to claim 1, 2, or 3 with which the remainder becomes 0.002 - 0.05% of N, and a list from Fe and an unescapable impurity O 0.05 to 0.5% 0.03 - 0.1% of C.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a R-Fe-B system rare earth permanent magnet ingredient.

[0002]

[Description of the Prior Art] The rare earth permanent magnet is used abundantly in the field of the electrical and electric equipment for outstanding magnetic properties and economical efficiency, and the high performance-ization is demanded increasingly in recent years. Among these rare earth permanent magnets, since Nd which is a main element existing in abundance from Sm

compared with a rare earth cobalt magnet, and Co are not used for a R-Fe-B system rare earth permanent magnet so much, its material cost is cheap, and it is the extremely excellent permanent magnet ingredient with which magnetic properties also easily endure a rare earth cobalt magnet.

[0003] For this reason, the further high property-ization of this R-Fe-B system rare earth permanent magnet is desired. In order to form a R-Fe-B system rare earth permanent magnet into a high property, it is required to reduce the oxygen density in an alloy. However, although abnormality grain growth tends to take place in a sintering process and Br is high when the oxygen density in an alloy is reduced, it becomes the bad magnet of square shape nature with inadequate (BH) max.

[0004] Even if this invention was made in view of the above-mentioned situation and reduces the oxygen density in an alloy, there is little abnormality grain growth, and it aims at offering a highly efficient R-Fe-B system rare earth permanent magnet ingredient.

[0005]

[The means for solving a technical problem and the gestalt of implementation of invention] In order that this invention person may attain the above-mentioned purpose, as a result of inquiring wholeheartedly, Co, aluminum, Cu, By distributing and depositing in homogeneity Zr compound detailed in the R-Fe-B system rare earth permanent magnet which contains Zr, Nb, or Hf in it, Nb compound, or Hf compound Grain growth of Nd system magnet alloy mainly manufactured at a hypoxia process was controlled, and it succeeded in obtaining the sintering permanent magnet ingredient which improved remarkably magnetic properties and sintering temperature width of face.

[0006] Furthermore, when it explains in full detail, in a R-Fe-B system rare earth permanent magnet, if the oxygen density in an alloy is reduced, abnormality grain growth will tend to take place, optimal sintering temperature width of face is also narrow, and productivity is very bad [width of face]. Then, minute amount addition of the new element was carried out at the alloy for the above-mentioned

problem solving, and the problem solving was tried.

[0007] As a result of studying wholeheartedly the alloying element newly added in the R-Fe-B system rare earth permanent magnet containing Cu, and its amount as JP,2000-234151,A proposed previously described, this invention person namely, by adding Zr in a minute amount Although it reported that it was possible to raise a residual magnetic flux density (Br) a little, and to make coercive force (iHc) increase sharply Furthermore, in order to aim at improvement in magnetic properties, when it strives for reduction of the oxygen density in a production process, by depositing minutely and uniformly a ZrB compound, a NbB compound, or a HfB compound in a magnet, the knowledge of an optimal sintering temperature field being remarkably expandable is carried out, and this invention is completed.

[0008] Hereafter, lessons is taken from this invention and it explains in more detail. The R-Fe-B system rare earth permanent magnet ingredient of this invention (however, R) one sort of rare earth elements or two sorts or more are shown. In the RFeB system magnet alloy whose $Fe_{14}R_2B$ phase's 1 which is main phase component's existence capacity percentage is 87.5 - 97.5% and whose oxide's of rare earth or rare earth, and transition metals existence capacity percentage is 0.1 - 3% The compound chosen from the ZrB compound which consists of Zr and B as a principal component all over the metal texture of this alloy, the NbB compound which consists of Nb and B, and the HfB compound which consists of Hf and B with the mean particle diameter of 5 micrometers or less And it is characterized by the maximum spacing between the ZrB compound which adjoins each other and exists in the above-mentioned alloy, a NbB compound, and the compound chosen from a HfB compound distributing to homogeneity by 50 micrometers or less.

[0009] If the above-mentioned RFeB system magnet alloy is described, the magnetic properties of a RFeB system magnet alloy increase a $Fe_{14}R_2B$ phase's 1 which discovers magnetism's existence capacity rate, it will be lessening nonmagnetic R rich grain boundary phase in inverse proportion to it, and

improvement in a residual magnetic flux density and an energy product will have been achieved. R rich phase cleans the grain boundary of a main phase Fe₁₄R₂B plane 1, and is bearing the role of generating coercive force, by removing the impurity and crystal defect of a grain boundary. Therefore, it becomes the main point on magnetic-properties development how much big coercive force is acquired how by being unable to lose R rich phase completely out of the organization of a magnet alloy, but utilizing little R rich phase as efficiently as possible, and making a grain boundary clean just because flux density becomes high. Generally, since R rich phase is activity, it will oxidize easily through grinding, a sintering process, etc., will form an R acid ghost phase, and will exhaust R rich phase. And if R rich phase adjusted a little is in process, reacts with oxygen and is consumed as an oxide, health of a grain boundary organization cannot be improved completely, but predetermined coercive force will no longer be acquired. The cure which obtains the big aperiodic compass of coercive force with a high residual magnetic flux density and which prevents oxidation of R rich phase through a production process in order in other words to acquire magnetic properties, using R rich phase of a critical mass effectively is needed. For this reason, in the newest high property Nd magnet production line, by carrying out, where each process of grinding, molding, and sintering is completely intercepted from oxygen, and lessening nonmagnetic Nd rich phase and the oxide of Nd as much as possible, the amount of magnetic phase Fe₁₄Nd₂B₁ is made [many / as possible], and improvement in magnetic properties is achieved.

[0010] However, reduction of Nd oxide phase abundance by such oxidation reaction prevention causes a new problem. It is generating of the abnormality growth grain in a sintering process.

[0011] At a sintering process, densification advances by the sintering reaction of fines. The cast fines are diffused joining mutually at sintering temperature, by eliminating the intervening hole outside, are filled up with the space in a sintered compact, and contract. Nd which lives together at this time -- it is said that the

rich liquid phase promotes a sintering reaction smoothly.

[0012] In the later stage of sintering, the hole which remains that a final consistency should be reached is diffused out of a system, and a sintered compact excludes it. Each crystal grain which sintering completed begins to grow up to be this final improvement in a consistency and coincidence with Ostwald growth. Itself is a lattice defect, the surface energy which a grain boundary has will decrease, the free energy of the whole sintered compact will fall, and the grain boundary which each crystal grain has will serve as stability, if the grain boundary die length per volume becomes small with growth.

[0013] Since in the case of a magnetic domain wall new chestnut ESHON mold magnet like a sintering Nd magnet coercive force generally becomes large so that the magnitude of crystal grain is small, a sintered compact with crystal grain small as much as possible is desirable. It will be thought of because a serious lattice defect's whose magnetic domain wall generating is attained in low magnetic field existence probability becomes high that coercive force becomes small as crystal grain becomes large, if crystal growth is carried out and the grain boundary area per grain increases.

[0014] Although it is predicted that the coercive force of Nd magnet becomes high, so that crystal grain becomes small to the single domain particle size of about 0.3 micrometers of Nd magnet which stops receiving effect in a lattice defect not much, even if small [by constraint of the stability of the grinding approach or fines, sintering conditions, etc. / in a rare earth sintered magnet / several micrometers] in the present condition at mean particle diameter, about 2-micrometer sintered compact mean particle diameter is considered to be a limitation.

[0015] As mentioned above, while densification with a final sintered compact advances, grain growth happens in the anaphase of a sintering process.

Although densification is required because of the improvement in flux density of a magnet, grain growth must be prevented for maintenance of coercive force. In the conventional Nd magnet, Nd oxide of a constant rate existed in 3 importance

of a grain boundary etc. as inclusion. Although this Nd oxide carried out pinning of the grain boundary migration accompanying crystal growth and consistency-ization of a sintered compact progressed, migration of a grain boundary, i.e., grain growth, was able to be suppressed.

[0016] The content of Nd is lessened, and since the abundance of Nd oxide is insufficient, it becomes impossible however, to fully demonstrate the pinning effectiveness in the high property Nd magnet which suppressed oxidation at a process further. For this reason, the phenomenon of huge abnormality growth grain generating in which specific crystal grain grows greatly rapidly at sintering temperature appears. Although the example is shown in the microphotography of drawing 20 (a) and (b), the crystal grain of the case where the crystal grain of the direction of orientation from the first becomes large as for the crystal grain which carried out abnormality growth in this way, and a different direction from the direction of orientation may grow.

[0017] Although the magnetic domain by the anchor effect is observed in drawing 20 (a) and (b), the directions of a magnetic domain wall differ for every abnormality growth grain 180 degrees, and it is understood that orientation is in disorder. Although orientation does not change, in addition to coercive force, the residual magnetic flux density is also decreasing with the grain with which coercive force is decreasing and with which, as for the crystal grain which has become large [a grain], orientation has also been in disorder. As a result, the hysteresis curve of the magnet obtained serves as inferior magnetic properties with bad square shape nature.

[0018] The greatest spacing which is 5 micrometers or less as that deposit mean particle diameter, and adjoins [trouble / in this high property magnet manufacture] each other in an alloy again in the compound chosen from the ZrB compound with which this invention person consists of Zr and B as a principal component, the NbB compound which consists of Nb and B, and the HfB compound which consists of Hf and B, and deposits was solved by distributing homogeneity by 50 micrometers or less. That is, grain growth of a sintered

compact was able to be suppressed very effectively by uniform distribution of such a ZrB compound, a NbB compound, or a HfB compound. When it has an R acid ghost and the effectiveness more than equivalent even if the grain boundary pinning effectiveness of a ZrB compound, a NbB compound, and a HfB compound is 5 micrometers or less in small magnitude, and the greatest spacing which adjoins each other and deposits makes homogeneity distribute this by 50 micrometers or less, grain growth can be effectively suppressed in an amount smaller than an R acid ghost. The huge abnormality growth grain of the Fe₁₄R₂B plane 1 from which it becomes possible from which to control generating of a huge abnormality growth grain in a large sintering temperature requirement, and particle size has become 100 micrometers or more according to the effectiveness of such a ZrB compound, a NbB compound, and a HfB compound can be made into 3% or less at an existence capacity rate to the whole metal texture.

[0019] As mentioned above, the rare earth permanent magnet ingredient of this invention The Fe₁₄R₂B plane's 1 which is main phase component's existence capacity percentage is 87.5% to 97.5%. And it sets to the high property RFeB system magnet alloy whose oxide's which consists of rare earth or rare earth, and transition metals again existence capacity percentage is 0.1% to 3%. The compound chosen from the ZrB compound which consists of Zr and B as a principal component all over the metal texture of this alloy, the NbB compound which consists of Nb and B, and the HfB compound which consists of Hf and B is 5 micrometers or less as the deposit mean particle diameter. And the greatest spacing which adjoins each other in the above-mentioned alloy again, and deposits is distributing to homogeneity by 50 micrometers or less, and it sets into this rare earth permanent magnet ingredient in this case. It is suitable that the huge abnormality growth grain of a Fe₁₄R₂B plane 1 with which particle size is 100 micrometers or more is 3% or less at an existence capacity rate to the whole metal texture.

[0020] The above-mentioned rare earth permanent magnet alloy is weight percent as the presentation here. Especially R= 27 to 33% 28.8-31.5%Co=0.1-

10%, Especially B= 0.9 to 1.5% 1.3 to 3.4% 0.95-1.15%aluminum=0.05-1.0%, especially -- 0.1 - 0.5%Cu= -- element = especially chosen from Zr, Nb, and Hf 0.05 to 0.3% 0.02 to 1.0% -- 0.02 to 1.0% It is especially desirable that it is [0.05 - 0.3%] what consists of the 0.002 - 0.04%Fe= remainder and also an unescapable impurity especially N= 0.002 to 0.05% 0.05 to 0.45% O= 0.05 to 0.5% 0.03 to 0.08% especially C= 0.03 to 0.1%.

[0021] Although it is shown here that R is one sort or two sorts or more in rare earth elements, it is desirable for it to be preferably chosen from Pr, Nd, Tb, Dy, and Ho, and to contain Nd in a principal component. especially -- under an alloy presentation and Nd -- 15 - 33wt% -- especially -- 18 - 33wt% -- containing is desirable. in this case, R mentioned above -- as -- 27 - 33wt% -- although contained, since there is a possibility that reduction in Br may become remarkable when there is a possibility that reduction in iHc may become [this] remarkable less than [27wt%] and 33wt% is exceeded, it is good to consider as 27 - 33wt%.

[0022] Although it is effective on Tc (Curie temperature) improvement effect to permute a part of Fe by Co in this invention, there is little effectiveness of Tc improvement of Co less than [0.1wt%], and it is good to consider as 0.1 - 10wt% in consideration of a cost side.

[0023] Since it has a possibility that reduction in Br may become remarkable when B has a possibility that reduction in iHc may become remarkable and 1.5wt% is exceeded, it is good to consider as 0.9 - 1.5wt% less than [0.9wt%].

[0024] aluminum is effective when raising coercive force (iHc), without applying cost, but since there is a possibility that reduction in Br may become large when there is very little effectiveness of the increment in iHc and it exceeds 1.0wt%, it is good to consider as 0.05 - 1.0wt% less than [0.05wt%].

[0025] Since Cu has a possibility that reduction in Br may become large when there is very little effectiveness of the increment in iHc and it exceeds 1.0wt%, it is good to consider as 0.02 - 1.0wt% less than [0.02wt%].

[0026] The element chosen from Zr, Nb, and Hf extends an optimal sintering

temperature field by compound addition with Cu, and effectiveness is in the increment in iHc in magnetic properties further. 0. Since there is a possibility that reduction in Br may become large when there is very little effectiveness of the increment in iHc and it exceeds 1.0wt%, it is good to consider as 0.02 - 1.0wt% less than [0.02wt%].

[0027] An oxygen content is good to consider as 0.05 - 0.5wt% less than [0.05wt%] in order to demonstrate the effectiveness as the effectiveness of depositing uniformly the ZrB compound of this invention, a NbB compound, and a HfB compound that existence of an oxide is the same, if square shape nature is not good and exceeds 0.5wt(s)% that it is easy to become fault sintering.

[0028] When square shape nature is not good and exceeds 0.1wt(s)% that it is easy to become fault sintering, a degree of sintering and its square shape nature are bad, and since a carbon content has a possibility of decreasing coercive force further, it is good [a carbon content] to consider as 0.03 - 0.1wt% less than [0.03wt%].

[0029] When square shape nature is not good and exceeds 0.05wt(s)% that it is easy to become fault sintering, a degree of sintering and its square shape nature are bad, and since a nitrogen content has a possibility of decreasing coercive force further, it is good [a nitrogen content] to consider as 0.002 - 0.05wt% less than [0.002wt%].

[0030] The alloy and mixture with Fe or aluminum which are used as a raw material are sufficient as Cu, Zr and Nb which are used for this invention, or Hf. Furthermore, the little existence of La, Ce, Sm, nickel, Mn, Si, calcium, Mg, S, P, W, Mo, Ta, Cr, Ga, and Ti not more than 0.2wt% which it is contained in a use raw material, or is mixed into a production process does not spoil the effectiveness of this invention.

[0031] After the permanent magnet ingredient of this invention obtains an alloy according to a conventional method using the ingredient of business as shown in the example mentioned later, it can be obtained by pulverizing by carrying out and heat-treating [cast, sinter and] a hydrogen treating and half-

dehydrogenation treatment if needed, and two alloying methods can be used for it, and it can also be used by making them a desired presentation.

[0032] In the fixed presentation range of R-Fe-B-Cu-Zr [which according to this invention uses a R-Fe-B-Cu system as the base and contains Zr of **** small quantity; Nb or Hf], Nb, or Hf system By heat-treating at alloy casting, grinding, molding, sintering, and temperature still lower than sintering temperature, make a residual magnetic flux density (Br) increase for a while, coercive force (iHc) is made to increase sharply, it excels in square shape nature, and 20-60 degrees C of optimal sintering temperature fields can be extended further.

[0033] Therefore, by Br, the magnetic properties shall have [10 or more kOes and square shape ratio $4x(BH)_{max}/Br^2$] more than 12.5G, and, as for the permanent magnet ingredient of this invention, coercive force iHc shall have 0.95 or more outstanding magnetic properties.

[0034]

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example. In addition, in the rare earth permanent magnet ingredient of the following example and the example of a comparison, an oxide's of the Fe₁₄R₂B plane's 1 existence capacity rate, rare earth or rare earth, and transition metals existence capacity rate and a huge abnormality growth grain's of Fe₁₄R₂B plane 1 with a particle size of 100 micrometers or more existence capacity rate are collectively shown in Table 13.

[0035] As a [example 1] start raw material, Nd, Pr, Dy, electrolytic iron, Co, ferroboration, aluminum and Cu, and ferro zirconium were used, and the alloy was obtained with the congruence chill roll method by the weight ratio as a comparison of the existence of Zr addition after blending with the presentation of 27Nd-2Pr-1 Dy-BAL.Fe-3Co-1B-0.5aluminum-0.2 Cu-XZr (0 X= 0.2). The hydrogen treating was performed for the obtained alloy in the hydrogen ambient atmosphere of +1.0**0.2 kgf/cm², and dehydrogenation treatment of 700 degree-Cx 5 hours was performed in the vacuum of 10 to 2 or less Torrs. The alloy

obtained at this time is hundreds of micrometers coarse powder by hydrogenation and dehydrogenation treatment. 0.08wt(s)% oleic acid was mixed with the obtained coarse powder by V mixer as lubricant, and it pulverized in mean particle diameter of about 3 micrometers with the jet mill in a nitrogen air current further. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 10kOe, casting by the pressure of 1.2 ton/cm² perpendicularly to the field, sintering those molding objects in Ar ambient atmosphere at 1,020 to 1,100 degrees C for 2 hours and cooling further, it heat-treated in Ar ambient atmosphere at 500 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.031-0.043, 0.009-0.017, and 0.105-0.186wt%, respectively.

[0036] The result of the acquired magnetic properties is shown in drawing 1 -3. Although what sintered Zr-less elegance (example of a comparison) at 1,020 degrees C and 1,040 degrees C is 0.954 and 0.955, respectively when sintering temperature and the relation of a square shape ratio are seen, and a square shape ratio is good, when Br is seen, 1,020 degrees C is 12.95kG(s), 1,040 degrees C is 13.24kG(s), and Br of 1,020-degree-C sinter is an inadequate value. This shows that the optimal sintering temperature of Zr-less elegance is only 1,040 degrees C. On the other hand, Zr addition article is good, without Br, iHc, and a square shape ratio hardly changing at 1,040 degrees C, 1,060 degrees C, and 1,080 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face. Furthermore, it turns out that the direction of Zr addition article is carrying out the increment in 1kOe by 100G and iHc by Br, and addition of Zr is excellent in the optimal sintering temperature.

[0037] Moreover, when the polarization image of the sintered compact of drawing 4 (a) and (b) is seen, it turns out that two about 500-micrometer abnormality grain growing regions have Zr-less elegance (a) in this field.

[0038] Furthermore, when the element distribution image by EPMA was seen, as

for Zr addition article, the ZrB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less, and, as for this ZrB compound, the quantitative analysis by EPMA showed that Zr and B were principal components.

[0039] By adding Zr and depositing a ZrB compound finely uniformly in a sintered compact from these things, shows having controlled abnormality grain growth and having expanded optimal sintering temperature width of face.

[0040] As a [example 2] start raw material, Nd, Tb, electrolytic iron, Co, ferroboron, aluminum and Cu, and ferro zirconium are used. As a comparison of the existence of Zr addition The ingot of each presentation was obtained by carrying out the RF dissolution and casting in a weight ratio to water-cooled copper mold after blending with the presentation of 30.0Nd-0.5 Tb-BAL.Fe-1Co-1.1B-0.7aluminum-0.1 Cu-XZr (3 0. X= 0.01, 1.2). Coarse grinding of these ingots was carried out by BURAUUMIRU, it processed with the jet mill in a nitrogen air current further, and fines with a mean particle diameter of about 3 micrometers were obtained. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 15kOe, casting by the pressure of 0.7 ton/cm² perpendicularly to the field, sintering the molding object of that in Ar ambient atmosphere at 1,020 to 1,100 degrees C for 2 hours and cooling further, it heat-treated in Ar ambient atmosphere at 600 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.081-0.092, 0.003 to 0.01, and 0.058-0.081wt%, respectively.

[0041] The result of the acquired magnetic properties is shown in drawing 5 -7. Although square shape ratios are 0.956 and 0.955, respectively and are good, if what sintered 0.01 Zr at 1,020 degrees C and 1,040 degrees C when sintering temperature and the relation of a square shape ratio were seen looks at Br, 1,020 degrees C will be 13.07kG(s), 1,040 degrees C will be 13.46kG(s), and Br of 1,020-degree-C sinter will tend to deteriorate. On the other hand, 0.3 Zr is

good, without Br, iHc, and a square shape ratio hardly changing at 1,040 degrees C, 1,060 degrees C, and 1,080 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face. furthermore -- although it turns out that Br, iHc, and a square shape ratio hardly change at 1,040 degrees C, 1,060 degrees C, and 1,080 degrees C, but 1.2 Zr has 40 degrees C of optimal sintering temperature width of face -- the direction of 0.3 Zr -- Br -- 13.60-13.66 -- it turns out that the magnetic properties of 15.0-15.5kOe are acquired by kG and iHc, and the direction of addition of 0.3 Zr is excellent.

[0042] Moreover, when the element distribution image by EPMA was seen, as for 0.3 Zr, the ZrB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. On the other hand, the ZrB compound 5 micrometers or less deposited at intervals of 50 micrometers or more, and the diameter was not [0.01 Zr] uniform a little compared with 0.3 Zr. Furthermore, although the ZrB compound 5 micrometers or less deposited at intervals of 50 micrometers or less, since 1.2 Zr had too many additions of Zr, its diameter suited to the inclination for magnetic properties to deteriorate compared with 0.3 Zr. Moreover, as for this ZrB compound, the quantitative analysis by EPMA showed that Zr and B were principal components.

[0043] These things show having controlled abnormality grain growth and having expanded optimal sintering temperature width of face, when a diameter deposits a ZrB compound 5 micrometers or less finely uniformly at intervals of 50 micrometers or less in a sintered compact.

[0044] The further high property-ization was tried by using two alloying methods for [example 3] this invention. In the following four examples 3-1, the example 3-2, the example 3-3, and the example 3-4, experiment conditions had changed only the presentation of a hardener and assistant **, and the hardener was produced with the single chill roll method, performed the hydrogen treating in the hydrogen ambient atmosphere of +0.5 - +2.0 kgf/cm², and performed half-dehydrogenation treatment of 500 degree-Cx 3 hours in the vacuum of 10 to 2 or less Torrs. Moreover, assistant ***** carried out the RF dissolution and obtained the ingot

by casting to water-cooled copper mold.

[0045] next, a hardener -- 90wt(s)% and assistant ** -- 10wt% weighing capacity -
- carrying out -- as lubricant -- zinc stearate -- 0.05wt(s)% -- it added, and mixed
by V mixer and fines with a mean particle diameter of about 4 micrometers were
further obtained with the jet mill in a nitrogen air current. Then, fill up the metal
mold of molding equipment with these fines, and orientation is carried out in the
field of 12kOe. It casts by the pressure of 0.5 ton/cm² perpendicularly to a field.
The molding object of that from 1,020 degrees C to 1,100 degrees C every 10
degrees C 2 hours, After sintering in the vacuum ambient atmosphere of 10 to 4
or less Torr and cooling further, it heat-treated in the vacuum ambient
atmosphere of 10 to 2 or less Torr at 500 degrees C for 1 hour, and the
permanent magnet ingredient of each presentation was obtained.

[0046] It was made the presentation of 30.0 Nd-BAL.Fe-4.6Co-1.4B-0.2
aluminum-XZr (0 X= 0.5) by the weight ratio, and three to example 1 hardener
made assistant ***** the presentation of 36.0Nd-10.2 Dy-BAL.Fe-25.8Co-
0.2aluminum-2.4Cu by the weight ratio. The presentation after mixing is 29.7Nd-
1.0 Dy-BAL.Fe-6.7Co-1.2B-0.2aluminum-0.24 Cu-XZr (0 X= 0.45).

[0047] It was made the presentation of 28.4 Nd-BAL.Fe-1.9Co-1.3B-0.4
aluminum-XZr (0 X= 0.4) by the weight ratio, and three to example 2 hardener
made assistant ***** the presentation of 36.9Nd-10.2 Tb-BAL.Fe-30.2Co-0.6B-
0.3aluminum-3.2Cu by the weight ratio. The presentation after mixing is 29.3Nd-
1.0 Tb-BAL.Fe-4.7Co-1.2B-0.4aluminum-0.32 Cu-XZr (0 X= 0.39).

[0048] It was made the presentation of 27.2 Nd-BAL.Fe-0.9Co-1.0B-0.2aluminum
by the weight ratio, and three to example 3 hardener made assistant ***** the
presentation of 50.1Nd-9.4 Dy-BAL.Fe-23.9Co-1.0B-0.2aluminum-1.1 Cu-XZr (0
X= 1.1) by the weight ratio. The presentation after mixing is 29.5Nd-0.9 Dy-
BAL.Fe-3.2Co-1.0B-0.2aluminum-0.1 Cu-XZr (0 X= 0.11).

[0049] It was made the presentation of 27.0Nd-1.0 Dy-BAL.Fe-4.6Co-1.3B-0.4
aluminum-XZr (0 X= 0.45) by the weight ratio, and three to example 4 hardener
made assistant ***** the presentation of 35.5Nd-9.8 Tb-BAL.Fe-29.0Co-

0.3aluminum-2.3 Cu-XZr (0 X= 0.45) by the weight ratio. Mixing mixed a Zr-less hardener, Zr-less assistant **, and a hardener with Zr and assistant ** with Zr, respectively. The presentation after mixing is 27.9Nd-2.3Dy-1.0 Tb-BAL.Fe-7.0Co-1.1B-0.4aluminum-0.2 Cu-XZr (0 X= 0.45).

[0050] The obtained result is shown in Tables 1-4. Tables 1-4 show what added Zr excelling [case / any / of an example 3-1, an example 3-2, an example 3-3, and an example 3-4] the additive-free thing in Br, iHc, and a square shape ratio, and having expanded, when an optimal sintering temperature field also adds Zr further.

[0051]

[Table 1]

実施例 3-1

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,050℃のみ	13.53	12.8	0.958
0.45	1,060～1,070℃	13.64～13.61	13.2～13.8	0.963～0.966

[0052]

[Table 2]

実施例 3-2

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,080℃のみ	13.45	12.5	0.957
0.39	1,060～1,080℃	13.53～13.61	13.3～13.8	0.959～0.964

[0053]

[Table 3]

実施例 3-3

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,080℃のみ	13.58	13.1	0.956
0.11	1,060～1,080℃	13.61～13.66	13.7～14.1	0.961～0.963

[0054]

[Table 4]

実施例 3-4

Zr 量	最適焼結温度領域	Br	iHc	角型比
0	1,080℃のみ	12.88	16.9	0.956
0.45	1,080～1,100℃	12.92～13.02	17.1～17.7	0.961～0.968

[0055] Furthermore, in any [of an example 3-1 an example 3-2, an example 3-3, and an example 3-4] case, when the element distribution image by EPMA was

seen, as for Zr addition article, the ZrB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Moreover, as for this ZrB compound, the quantitative analysis by EPMA showed that Zr and B were principal components.

[0056] These things show having added Zr also in two alloying methods, having controlled abnormality grain growth and having expanded optimal sintering temperature width of face by depositing a ZrB compound finely uniformly in a sintered compact.

[0057] As a [example 4] start raw material, Nd, Pr, Dy, electrolytic iron, Co, ferrobore, aluminum and Cu, and ferro NYUUBU were used, and the alloy was obtained with the congruence chill roll method by the weight ratio as a comparison of the existence of Nb addition after blending with the presentation of 26.5Nd-2.2Pr-2.5 Dy-BAL.Fe-4.5Co-1.1B-0.4aluminum-0.5 Cu-XNb (0 X= 0.2).

The hydrogen treating was performed for the obtained alloy in the hydrogen ambient atmosphere of $+1.5 \times 10^{-3}$ kgf/cm², and dehydrogenation treatment of 800 degree-Cx 5 hours was performed in the vacuum of 10 to 2 or less Torrs. The alloy obtained at this time is hundreds of micrometers coarse powder by hydrogenation and dehydrogenation treatment. 0.05wt(s)% zinc stearate was mixed with the obtained coarse powder by V mixer as lubricant, and it pulverized in mean particle diameter of about 3 micrometers with the jet mill in a nitrogen air current further. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 15kOe, casting by the pressure of 0.5 ton/cm² perpendicularly to the field, sintering those molding objects in Ar ambient atmosphere at 1,000 to 1,080 degrees C for 2 hours and cooling further, it heat-treated in Ar ambient atmosphere at 500 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.061-0.073, 0.019-0.027, and 0.095-0.116wt%, respectively.

[0058] The result of the acquired magnetic properties is shown in drawing 8 -10.

If sintering temperature and the relation of a square shape ratio are seen, what sintered Nb-less elegance at 1,000 degrees C and 1,020 degrees C is 0.951 and 0.955, respectively, its a square shape ratio is good, but when Br is seen, 1,000 degrees C is 12.87kG(s), 1,020 degrees C is 13.23kG(s), and Br of 1,000-degree-C sinter is an inadequate value. This shows that the optimal sintering temperature of Nb-less elegance is only 1,020 degrees C. On the other hand, Nb addition article is good, without Br, iHc, and a square shape ratio hardly changing at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face.

Furthermore, it turns out that the direction of Nb addition article is carrying out the increment in 500Oe by 80G and iHc by Br, and addition of Nb is excellent in the optimal sintering temperature.

[0059] Moreover, according to the polarization image of a sintered compact, it turned out that two about 500-micrometer abnormality grain growing regions have Nb-less elegance (a) in this field.

[0060] Furthermore, when the element distribution image by EPMA was seen, as for Nb addition article, the NbB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Moreover, as for this NbB compound, the quantitative analysis by EPMA showed that Nb and B were principal components.

[0061] By adding Nb and depositing a NbB compound finely uniformly in a sintered compact from these things, shows having controlled abnormality grain growth and having expanded optimal sintering temperature width of face.

[0062] As a [example 5] start raw material, Nd, Tb, electrolytic iron, Co, ferroboron, aluminum and Cu, and ferro NYUUBU are used. As examination of Nb addition The ingot of each presentation was obtained by carrying out the RF dissolution and casting in a weight ratio to water-cooled copper mold after blending with the presentation of 29.1Nd-0.2 Tb-BAL.Fe-2.7Co-1.2B-0.4aluminum-0.5 Cu-XNb (57 0. X= 0.01, 1.15). Coarse grinding of these ingots was carried out by BURAUMMIRU, it processed with the jet mill in a nitrogen air

current further, and fines with a mean particle diameter of about 5 micrometers were obtained. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 12kOe, casting by the pressure of 1.2 ton/cm² perpendicularly to the field, sintering the molding object of that in the vacuum ambient atmosphere of 10 to 4 or less Torr at 1,000 to 1,080 degrees C for 2 hours and cooling further, it heat-treated in the vacuum ambient atmosphere of 10 to 2 or less Torr at 500 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.030-0.038, 0.027-0.041, and 0.328-0.418wt%, respectively.

[0063] The result of the acquired magnetic properties is shown in drawing 11 -13. Although square shape ratios are 0.951 and 0.953, respectively and are good, if what sintered 0.01 Nb(s) at 1,000 degrees C and 1,020 degrees C when sintering temperature and the relation of a square shape ratio were seen looks at Br, 1,000 degrees C will be 13.37kG(s), 1,020 degrees C will be 13.55kG(s), and Br of 1,000-degree-C sinter will tend to deteriorate. On the other hand, 0.57 Nb(s) are good, without Br, iHc, and a square shape ratio hardly changing at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face. furthermore -- although it turns out that Br, iHc, and a square shape ratio hardly change at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, but 1.15 Nb(s) have 40 degrees C of optimal sintering temperature width of face -- the direction of 0.57 Nb(s) -- Br -- 13.65-13.67 -- it turns out that the magnetic properties of 14.9-15.2kOe are acquired by kG and iHc, and the direction of addition of 0.57 Nb(s) is excellent.

[0064] Moreover, when the element distribution image by EPMA was seen, as for 0.57 Nb(s), the NbB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Furthermore, although the NbB compound 5 micrometers or less deposited [the diameter] at intervals of 50

micrometers or less, since 1.15 Nb(s) had too many additions of Nb, magnetic properties suited its low inclination compared with 0.57 Nb(s). Moreover, as for this NbB compound, the quantitative analysis by EPMA showed that Nb and B were principal components.

[0065] These things show having controlled abnormality grain growth and having expanded optimal sintering temperature width of face, when a diameter deposits a NbB compound 5 micrometers or less finely uniformly at intervals of 50 micrometers or less in a sintered compact.

[0066] The further high property-ization was tried by using two alloying methods for [example 6] this invention. In the following four examples 6-1, the example 6-2, the example 6-3, and the example 6-4, experiment conditions had changed only the presentation of a hardener and assistant **, and the hardener was produced with the single chill roll method, performed the hydrogen treating in the hydrogen ambient atmosphere of +0.5 - +2.0 kgf/cm², and performed half-dehydrogenation treatment of 500 degree-Cx 3 hours in the vacuum of 10 to 2 or less Torrs.

Moreover, assistant ***** carried out the RF dissolution and obtained the ingot by casting to water-cooled copper mold.

[0067] next, a hardener -- 92wt(s)% and assistant ** -- 8wt% weighing capacity -- carrying out -- as lubricant -- zinc stearate -- 0.05wt(s)% -- it added, and mixed by V mixer and fines with a mean particle diameter of about 4 micrometers were further obtained with the jet mill in a nitrogen air current. Then, fill up the metal mold of molding equipment with these fines, and orientation is carried out in the field of 12kOe. It casts by the pressure of 0.5 ton/cm² perpendicularly to a field. The molding object of that from 1,020 degrees C to 1,100 degrees C every 10 degrees C 2 hours, After sintering in the vacuum ambient atmosphere of 10 to 4 or less Torrs and cooling further, it heat-treated at 500 degrees C for 1 hour in Ar gas ambient atmosphere of 10 to 2 or less Torrs, and the permanent magnet ingredient of each presentation was obtained.

[0068] It was made the presentation of 27.9 Nd-BAL.Fe-7.3Co-1.3B-0.2 aluminum-XNb (0 X= 0.4) by the weight ratio, and six to example 1 hardener

made assistant ***** the presentation of 36.0Nd-10.2 Dy-BAL.Fe-25.8Co-0.2aluminum-2.4Cu by the weight ratio. The presentation after mixing is 28.6Nd-3.1 Dy-BAL.Fe-8.8Co-1.2B-0.2aluminum-0.2 Cu-XNb (0 X= 0.4).

[0069] It was made the presentation of 28.1Nd-1.2 Tb-BAL.Fe-3.7Co-1.2B-0.4 aluminum-XNb (0 X= 0.7) by the weight ratio, and six to example 2 hardener made assistant ***** the presentation of 36.9Nd-10.2 Tb-BAL.Fe-30.2Co-0.6B-0.3aluminum-3Cu by the weight ratio. The presentation after mixing is 28.8Nd-2.0 Tb-BAL.Fe-5.8Co-1.1B-0.4aluminum-0.3 Cu-XNb (0 X= 0.7).

[0070] It was made the presentation of 27.2 Nd-BAL.Fe-0.9Co-1.0B-0.2aluminum by the weight ratio, and six to example 3 hardener made assistant ***** the presentation of 47.2Nd-8.9Dy-8.7 Tb-BAL.Fe-22.5Co-0.1aluminum-1.4 Cu-XNb (0 X= 1.0) by the weight ratio. The presentation after mixing is 28.8Nd-0.7Dy-0.7 Tb-BAL.Fe-2.7Co-1.0B-0.2aluminum-0.1 Cu-XNb (0 X= 0.1).

[0071] It was made the presentation of 27.0Nd-2.5 Dy-BAL.Fe-4.6Co-1.3B-0.4 aluminum-XNb (0 X= 0.4) by the weight ratio, and six to example 4 hardener made assistant ***** the presentation of 35.5Nd-9.8 Tb-BAL.Fe-29.0Co-0.3aluminum-2.3 Cu-XNb (0 X= 0.4) by the weight ratio. Mixing mixed a Nb-less hardener, Nb-less assistant **, and a hardener with Nb and assistant ** with Nb, respectively. The presentation after mixing is 27.7Nd-2.3Dy-0.8 Tb-BAL.Fe-6.6Co-1.2B-0.4aluminum-0.2 Cu-XNb (0 X= 0.4).

[0072] The obtained result is shown in Tables 5-8. Tables 5-8 show what added Nb excelling [case / any / of an example 6-1, an example 6-2, an example 6-3, and an example 6-4] the additive-free thing in Br, iHc, and a square shape ratio, and having expanded, when an optimal sintering temperature field also adds Nb further.

[0073]

[Table 5]

実施例 6-1

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,040℃のみ	13.24	16.8	0.962
0.4	1,040~1,080℃	13.28~13.33	16.6~16.8	0.961~0.965

[0074]

[Table 6]

実施例 6-2

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.46	15.5	0.954
0.7	1,030～1,070℃	13.54～13.61	16.3～16.8	0.965～0.969

[0075]

[Table 7]

実施例 6-3

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.58	15.1	0.951
0.1	1,030～1,070℃	13.61～13.66	15.9～16.5	0.961～0.967

[0076]

[Table 8]

実施例 6-4

Nb 量	最適焼結温度領域	Br	iHc	角型比
0	1,040℃のみ	13.56	14.8	0.959
0.4	1,040～1,080℃	13.65～13.72	15.5～16.1	0.967～0.970

[0077] Furthermore, in any [of an example 6-1 an example 6-2, an example 6-3, and an example 6-4] case, when the element distribution image by EPMA was seen, as for Nb addition article, the NbB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Moreover, as for this NbB compound, the quantitative analysis by EPMA showed that Nb and B were principal components.

[0078] These things show having added Nb also in two alloying methods, having controlled abnormality grain growth and having expanded optimal sintering temperature width of face by depositing a NbB compound finely uniformly in a sintered compact.

[0079] As a [example 7] start raw material, Nd, Pr, Tb, electrolytic iron, Co, ferrobore, aluminum and Cu, and FERROHAFU nium were used, and the alloy was obtained with the congruence chill roll method by the weight ratio as a comparison of the existence of Hf addition after blending with the presentation of 28.5Nd-1.0Pr-0.5 Tb-BAL.Fe-4.0Co-1.3B-0.4aluminum-0.5 Cu-XHf (0 X= 0.4). The hydrogen treating was performed for the obtained alloy in the hydrogen ambient atmosphere of +2.0**0.5 kgf/cm², and dehydrogenation treatment of 400

degree-Cx 3 hours was performed in the vacuum of 10 to 2 or less Torrs. The alloy obtained at this time is hundreds of micrometers coarse powder by hydrogenation and dehydrogenation treatment. 0.05wt(s)% Safi Norian was mixed with the obtained coarse powder by V mixer as lubricant, and it pulverized in mean particle diameter of about 5 micrometers with the jet mill in a nitrogen air current further. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 12kOe, casting by the pressure of 1.0 ton/cm² perpendicularly to the field, sintering those molding objects in Ar ambient atmosphere at 1,000 to 1,080 degrees C for 2 hours and cooling further, it heat-treated in Ar ambient atmosphere at 500 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.051-0.063, 0.029-0.037, and 0.135-0.216wt%, respectively.

[0080] The result of the acquired magnetic properties is shown in drawing 14 -16. If sintering temperature and the relation of a square shape ratio are seen, what sintered Hf-less elegance at 1,000 degrees C and 1,020 degrees C is 0.951 and 0.955, respectively, its a square shape ratio is good, but when Br is seen, 1,000 degrees C is 12.93kG(s), 1,020 degrees C is 13.43kG(s), and Br of 1,000-degree-C sinter is an inadequate value. This shows that the optimal sintering temperature of Hf-less elegance is only 1,020 degrees C. On the other hand, Hf addition article is good, without Br, iHc, and a square shape ratio hardly changing at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face.

Furthermore, it turns out that the direction of Hf addition article is carrying out the increment in 700Oe by 80G and iHc by Br, and addition of Hf is excellent in the optimal sintering temperature.

[0081] Moreover, when the polarization image of a sintered compact was seen, it turned out that two about 500-micrometer abnormality grain growing regions have Hf-less elegance (a) in this field.

[0082] Furthermore, when the element distribution image by EPMA was seen, as for Hf addition article, the HfB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Moreover, as for this HfB compound, the quantitative analysis by EPMA showed that Hf and B were principal components.

[0083] By adding Hf and depositing a HfB compound finely uniformly in a sintered compact from these things, shows having controlled abnormality grain growth and having expanded optimal sintering temperature width of face.

[0084] As a [example 8] start raw material, Nd, Pr, Dy, electrolytic iron, Co, ferroboron, aluminum and Cu, and FERROHAFU nium are used. As examination of Hf addition The ingot of each presentation was obtained by carrying out the RF dissolution and casting in a weight ratio to water-cooled copper mold after blending with the presentation of 28.7Nd-2.2Pr-1.2 Dy-BAL.Fe-3.6Co-1.2B-0.4aluminum-0.5 Cu-XHf (41 0. X= 0.01, 1.22). Coarse grinding of these ingots was carried out by BURAUUMIRU, it processed with the jet mill in a nitrogen air current further, and fines with a mean particle diameter of about 5 micrometers were obtained. Then, after filled up the metal mold of molding equipment with these fines, carrying out orientation in the field of 15kOe, casting by the pressure of 0.7 ton/cm² perpendicularly to the field, sintering the molding object of that in Ar ambient atmosphere at 1,000 to 1,080 degrees C for 2 hours and cooling further, it heat-treated in Ar ambient atmosphere at 600 degrees C for 1 hour, and the permanent magnet ingredient of each presentation was obtained. In addition, the carbon in these R-Fe-B system permanent magnet ingredients, nitrogen, and an oxygen content were 0.031-0.041, 0.023-0.040, and 0.228-0.411wt%, respectively.

[0085] The result of the acquired magnetic properties is shown in drawing 17 -19. Although square shape ratios are 0.951 and 0.953, respectively and are good, if what sintered 0.01 Hf(s) at 1,000 degrees C and 1,020 degrees C when sintering temperature and the relation of a square shape ratio were seen looks at Br, 1,000 degrees C will be 12.93kG(s), 1,020 degrees C will be 13.35kG(s), and Br

of 1,000-degree-C sinter will tend to deteriorate. On the other hand, 0.41 Hf(s) are good, without Br, iHc, and a square shape ratio hardly changing at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, and it turns out that there are 40 degrees C of optimal sintering temperature width of face. furthermore -- although it turns out that Br, iHc, and a square shape ratio hardly change at 1,020 degrees C, 1,040 degrees C, and 1,060 degrees C, but 1.22 Hf(s) have 40 degrees C of optimal sintering temperature width of face -- the direction of 0.41 Hf(s) -- Br -- 13.45-13.47 -- it turns out that the magnetic properties of 13.2-13.5kOe are acquired by kG and iHc, and the direction of addition of 0.41 Hf(s) is excellent.

[0086] Moreover, when the element distribution image by EPMA was seen, as for 0.41 Hf(s), the HfB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less. Furthermore, although the HfB compound 5 micrometers or less deposited [the diameter] at intervals of 50 micrometers or less, since 1.22 Hf(s) had too many additions of Hf, they were understood that magnetic properties are low compared with 0.41 Hf(s). Moreover, as for this HfB compound, the quantitative analysis by EPMA showed that Hf and B were principal components.

[0087] These things show having controlled abnormality grain growth and having expanded optimal sintering temperature width of face, when a diameter deposits a HfB compound 5 micrometers or less finely uniformly at intervals of 50 micrometers or less in a sintered compact.

[0088] The further high property-ization was tried by using two alloying methods for [example 9] this invention. In the following four examples 9-1, the example 9-2, the example 9-3, and the example 9-4, experiment conditions had changed only the presentation of a hardener and assistant **, and the hardener was produced with the single chill roll method, performed the hydrogen treating in the hydrogen ambient atmosphere of +0.5 - +2.0 kgf/cm², and performed half-dehydrogenation treatment of 500 degree-Cx 3 hours in the vacuum of 10 to 2 or less Torrs.

Moreover, assistant ***** carried out the RF dissolution and obtained the ingot

by casting to water-cooled copper mold.

[0089] next, a hardener -- 88wt(s)% and assistant ** -- 12wt% weighing capacity -
- carrying out -- as lubricant -- zinc stearate -- 0.05wt(s)% -- it added, and mixed
by V mixer and fines with a mean particle diameter of about 4 micrometers were
further obtained with the jet mill in a nitrogen air current. Then, fill up the metal
mold of molding equipment with these fines, and orientation is carried out in the
field of 12kOe. It casts by the pressure of 0.5 ton/cm² perpendicularly to a field.
The molding object of that from 1,020 degrees C to 1,100 degrees C every 10
degrees C 2 hours, After sintering in the vacuum ambient atmosphere of 10 to 4
or less Torr and cooling further, it heat-treated in the vacuum ambient
atmosphere of 10 to 2 or less Torr at 500 degrees C for 1 hour, and the
permanent magnet ingredient of each presentation was obtained.

[0090] It was made the presentation of 27.2 Nd-BAL.Fe-0.9Co-1.0B-0.2aluminum
by the weight ratio, and nine to example 1 hardener made assistant ***** the
presentation of 49.6Nd-9.3-Dy-BAL.Fe-23.6Co-0.2aluminum-1.1 Cu-XHf (0 X=
0.2) by the weight ratio. The presentation after mixing is 29.9Nd-1.1 Dy-BAL.Fe-
3.7Co-1.0B-0.2aluminum-0.1 Cu-XHf (0 X= 0.2).

[0091] It was made the presentation of 28.0Nd-2.5-Dy-BAL.Fe-4.6Co-1.3B-
0.4aluminum by the weight ratio, and nine to example 2 hardener made assistant
***** the presentation of 34.0Nd-9.4 Tb-BAL.Fe-27.8Co-0.3aluminum-2.2 Cu-
XHf (0 X= 8.4) by the weight ratio. The presentation after mixing is 28.7Nd-
2.2Dy-1.1 Tb-BAL.Fe-7.4Co-1.1B-0.4aluminum-0.3 Cu-XHf (0 X= 1.0).

[0092] It was made the presentation of 28.0Nd-1.3 Dy-BAL.Fe-7.3Co-1.3B-
0.2aluminum-0.5 Cu-XHf (0 X= 0.7) by the weight ratio, and nine to example 3
hardener made assistant ***** the presentation of 36.0Nd-10.2 Dy-BAL.Fe-
25.8Co-0.2aluminum-2.4Cu by the weight ratio. The presentation after mixing is
29.0Nd-2.3 Dy-BAL.Fe-9.5Co-1.2B-0.2aluminum-0.7 Cu-XHf (0 X= 0.7).

[0093] It was made the presentation of 27.0Nd-1.2 Tb-BAL.Fe-3.7Co-1.2B-
0.4aluminum-0.3 Cu-XHf (0 X= 0.7) by the weight ratio, and nine to example 4
hardener made assistant ***** the presentation of 36.9Nd-10.2 Tb-BAL.Fe-

30.2Co-0.3aluminum-3.3Cu-0.7Hf by the weight ratio. The presentation after mixing is 28.2Nd-2.3 Tb-BAL.Fe-6.9Co-1.1B-0.4aluminum-0.7 Cu-XHf (0 X= 0.7).

[0094] The obtained result is shown in Tables 9-12. Tables 9-12 show what added Hf excelling [case / any / of an example 9-1, an example 9-2, an example 9-3, and an example 9-4] the additive-free thing in Br, iHc, and a square shape ratio, and having expanded, when an optimal sintering temperature field also adds Hf further.

[0095]

[Table 9]

実施例 9-1

Hf 量	最適焼結温度領域	Br	iHc	角型比
0	1,020℃のみ	13.43	14.8	0.955
0.2	1,020～1,060℃	13.48～13.59	15.2～15.8	0.961～0.965

[0096]

[Table 10]

実施例 9-2

Hf 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	12.85	17.5	0.952
1.0	1,030～1,070℃	12.91～13.01	18.3～18.8	0.962～0.964

[0097]

[Table 11]

実施例 9-3

Hf 量	最適焼結温度領域	Br	iHc	角型比
0	1,030℃のみ	13.18	16.1	0.956
0.7	1,030～1,070℃	13.31～13.36	16.7～17.1	0.964～0.968

[0098]

[Table 12]

実施例 9-4

Hf 量	最適焼結温度領域	Br	iHc	角型比
0	1,020℃のみ	13.16	16.8	0.951
0.7	1,020～1,060℃	13.25～13.32	17.5～18.1	0.966～0.969

[0099] Furthermore, in any [of an example 9-1 an example 9-2, an example 9-3, and an example 9-4] case, when the element distribution image by EPMA was seen, as for Hf addition article, the HfB compound 5 micrometers or less deposited [the diameter] finely uniformly at intervals of 50 micrometers or less.

Moreover, as for this HfB compound, the quantitative analysis by EPMA showed that Hf and B were principal components.

[0100] These things show having added Hf also in two alloying methods, having controlled abnormality grain growth and having expanded optimal sintering temperature width of face by depositing a HfB compound finely uniformly in a sintered compact.

[0101] In addition, carrying out the RF dissolution of the assistant *****, and casting and carrying out hydrogenation and half dehydrogenation treatment to water-cooled mold or single **'s producing assistant ***** with a congruence chill roll method, and it carrying out hydrogenation and half dehydrogenation treatment, and the approach of single ** producing assistant ***** with a congruence chill roll method, and carrying out coarse grinding by BURAUUMIRU etc. are also effective in this invention.

[0102]

[Table 13]

		Fe ₁₄ R ₂ B ₁ (%)	酸化物(%)	異常成長粒(%)
実施例 1	Zr 0(比較例)	93.2	2.2	3.9
	Zr 0.2	93.1	2.1	0.5
実施例 2	Zr 0.01	94.1	0.9	4.0
	Zr 0.3	94.2	0.8	1.3
	Zr 1.2	93.7	1.0	1.4
実施例 3-1	Zr 0(比較例)	95.0	1.1	4.1
	Zr 0.45	95.0	1.0	0.5
実施例 3-2	Zr 0(比較例)	94.8	0.6	5.2
	Zr 0.39	94.4	0.5	1.3
実施例 3-3	Zr 0(比較例)	96.8	2.0	3.5
	Zr 0.11	96.7	2.1	0.8
実施例 3-4	Zr 0(比較例)	89.1	0.2	3.9
	Zr 0.45	89.2	0.1	2.0
実施例 4	Nb 0(比較例)	94.2	1.2	4.9
	Nb 0.2	94.1	1.1	0.8
実施例 5	Nb 0.01	91.1	1.9	5.0
	Nb 0.57	91.2	1.8	1.7
	Nb 1.15	90.2	2.0	1.7
実施例 6-1	Nb 0(比較例)	92.0	2.1	4.5
	Nb 0.4	92.1	2.0	0.9
実施例 6-2	Nb 0(比較例)	94.7	0.4	5.1
	Nb 0.7	94.6	0.3	1.0
実施例 6-3	Nb 0(比較例)	95.8	1.0	3.8
	Nb 0.1	95.7	1.1	1.8
実施例 6-4	Nb 0(比較例)	88.1	1.2	3.5
	Nb 0.4	88.2	1.1	1.0
実施例 7	Hf 0(比較例)	91.2	2.2	4.9
	Hf 0.4	91.1	2.1	0.7
実施例 8	Hf 0.01	94.8	1.9	5.0
	Hf 0.41	94.9	1.8	0.3
	Hf 1.22	94.0	2.0	0.4
実施例 9-1	Hf 0(比較例)	88.0	1.6	5.1
	Hf 0.2	88.0	1.7	1.5
実施例 9-2	Hf 0(比較例)	91.3	2.6	4.2
	Hf 1.0	91.4	2.5	1.1
実施例 9-3	Hf 0(比較例)	96.8	1.0	3.7
	Hf 0.7	96.9	1.1	0.5
実施例 9-4	Hf 0(比較例)	90.1	0.3	3.3
	Hf 0.7	90.0	0.4	1.0

[0103]

[Effect of the Invention] According to this invention, the R-Fe-B system rare earth permanent magnet ingredient of a high property can be obtained.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the relation between the sintering temperature of Zr-less elegance and elegance with Zr in an example 1, and a square shape ratio.

[Drawing 2] It is the graph which shows the relation between the sintering temperature of Zr-less elegance and elegance with Zr in an example 1, and iHc.

[Drawing 3] It is the graph which shows the relation between the sintering temperature of Zr-less elegance and elegance with Zr in an example 1, and Br.

[Drawing 4] It is the polarization image of Zr-less elegance (a) and elegance with Zr (b) in an example 1.

[Drawing 5] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Zr and the different square shape ratio in an example 2.

[Drawing 6] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Zr and different iHc in an example 2.

[Drawing 7] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Zr and different Br in an example 2.

[Drawing 8] It is the graph which shows the relation between the sintering temperature of Nb-less elegance and elegance with Nb in an example 4, and a square shape ratio.

[Drawing 9] It is the graph which shows the relation between the sintering temperature of Nb-less elegance and elegance with Nb in an example 4, and iHc.

[Drawing 10] It is the graph which shows the relation between the sintering

temperature of Nb-less elegance and elegance with Nb in an example 4, and Br.

[Drawing 11] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Nb(s) and the different square shape ratio in an example 5.

[Drawing 12] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Nb(s) and different iHc in an example 5.

[Drawing 13] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Nb(s) and different Br in an example 5.

[Drawing 14] It is the graph which shows the relation between the sintering temperature of Hf-less elegance and elegance with Hf in an example 7, and a square shape ratio.

[Drawing 15] It is the graph which shows the relation between the sintering temperature of Hf-less elegance and elegance with Hf in an example 7, and iHc.

[Drawing 16] It is the graph which shows the relation between the sintering temperature of Hf-less elegance and elegance with Hf in an example 7, and Br.

[Drawing 17] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Hf(s) and the different square shape ratio in an example 8.

[Drawing 18] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Hf(s) and different iHc in an example 8.

[Drawing 19] It is the graph which shows the relation of the different sintering temperature of the alloy of the amount of Hf(s) and different Br in an example 8.

[Drawing 20] (a) and (b) are microphotographies in which the huge abnormality growth grain in the conventional example is shown, respectively.

[Translation done.]

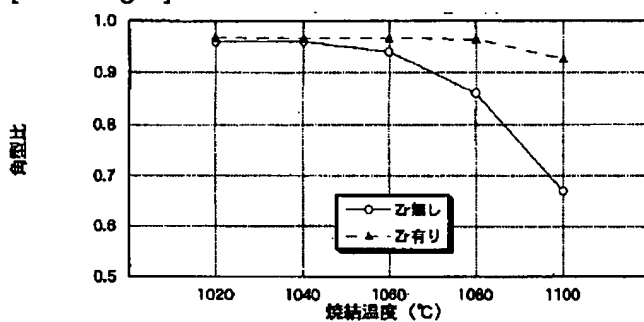
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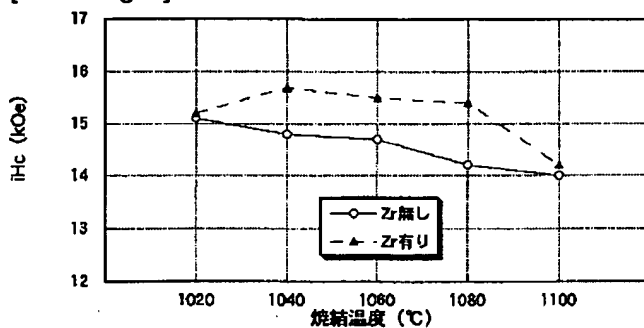
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DRAWINGS

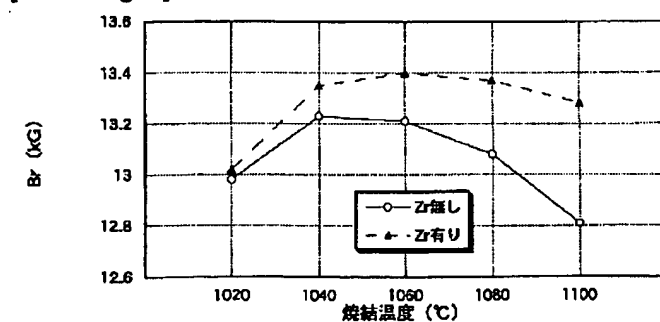
[Drawing 1]



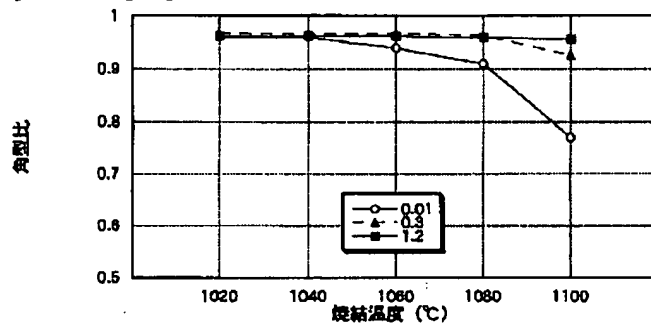
[Drawing 2]



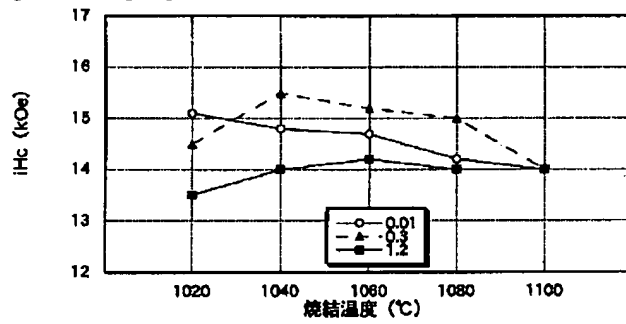
[Drawing 3]



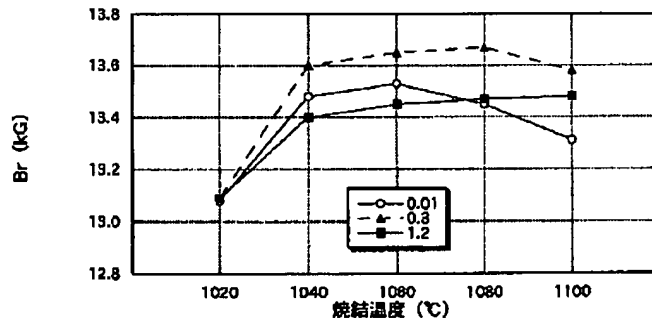
[Drawing 5]



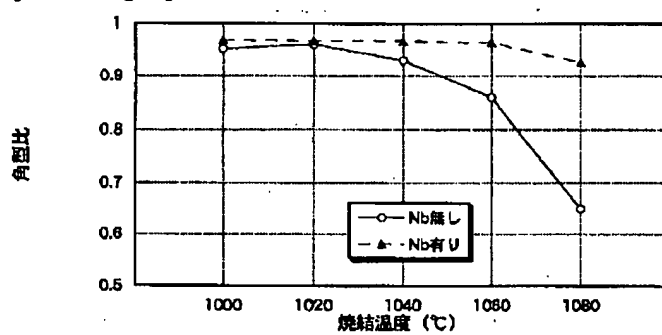
[Drawing 6]



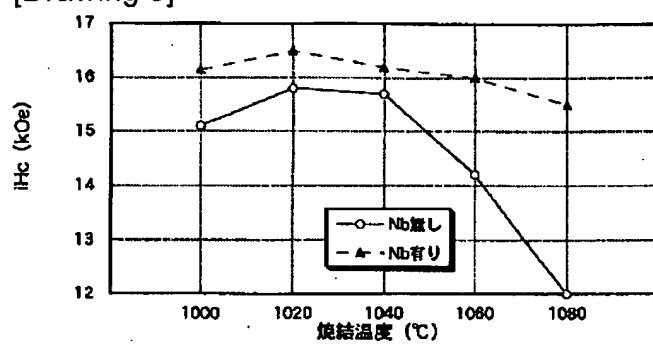
[Drawing 7]



[Drawing 8]

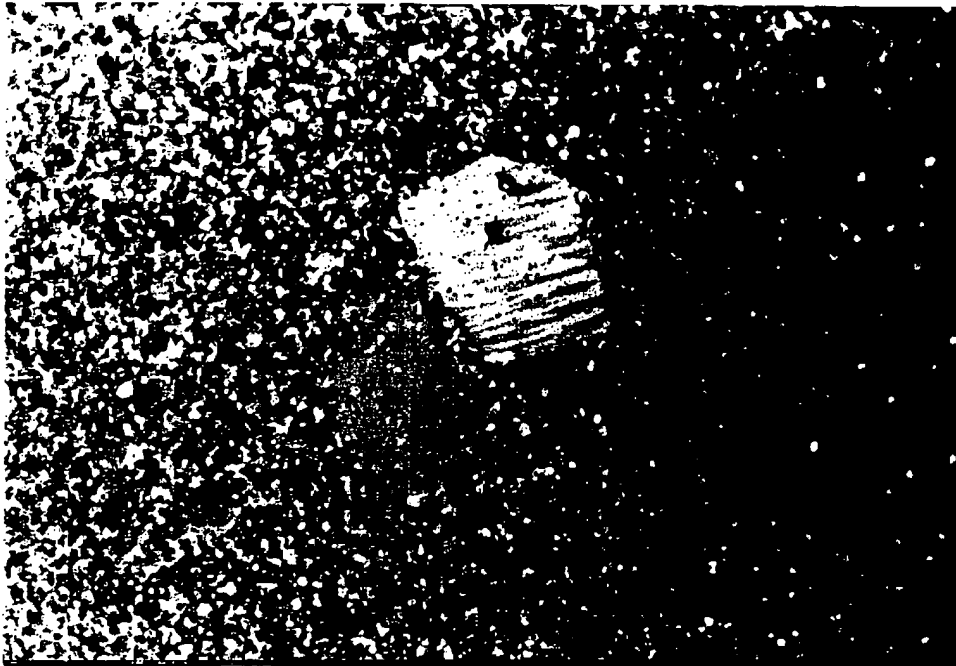


[Drawing 9]

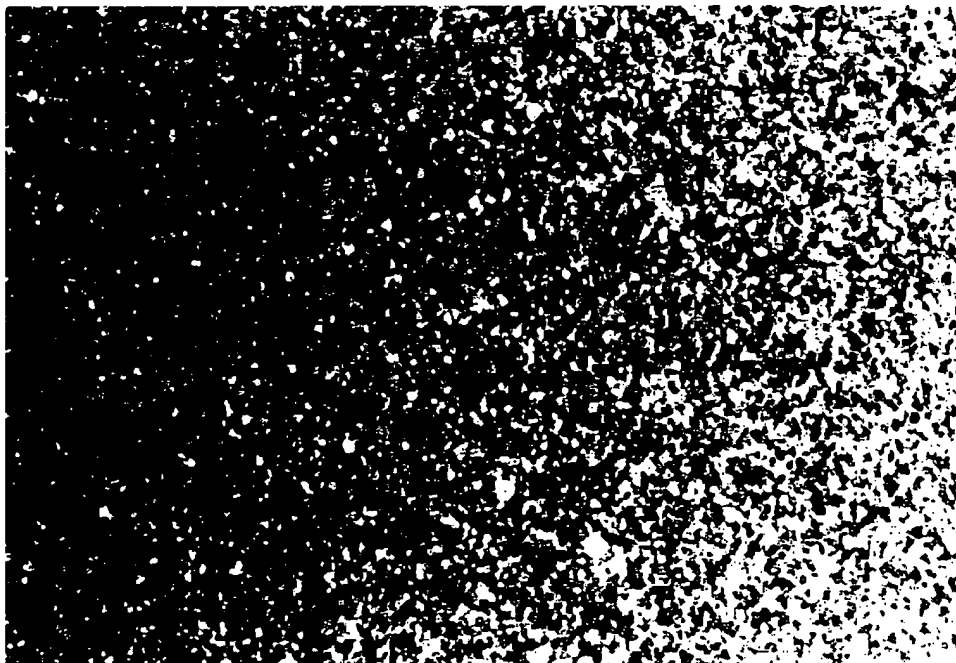


[Drawing 4]

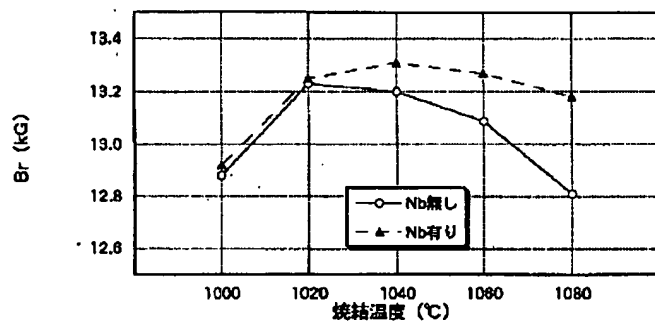
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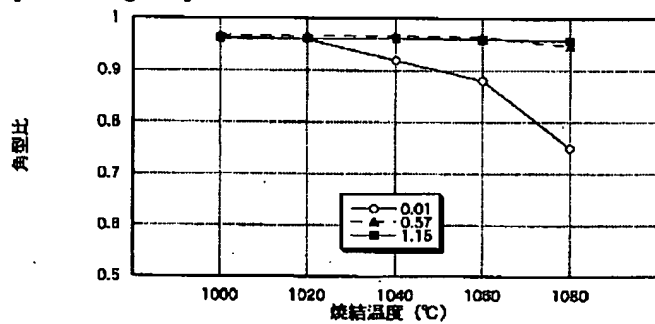
(b)



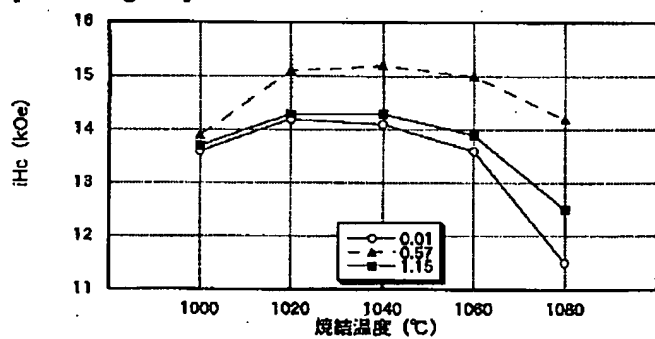
[Drawing 10]



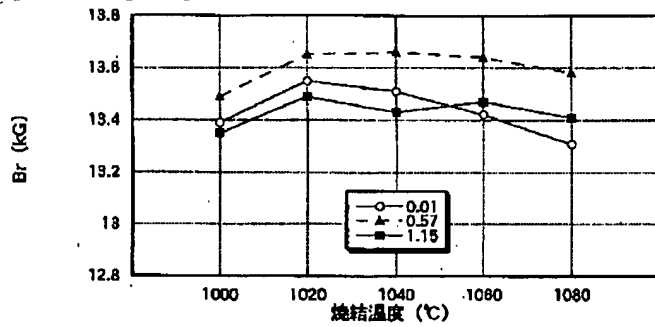
[Drawing 11]



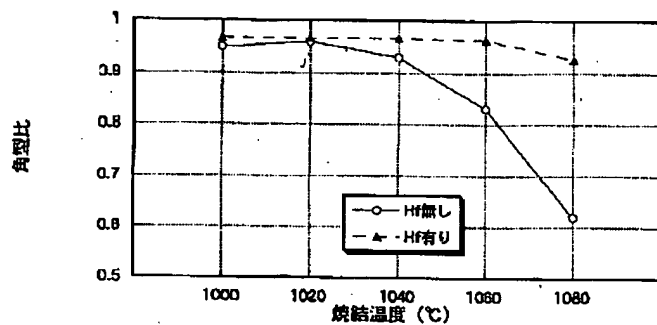
[Drawing 12]



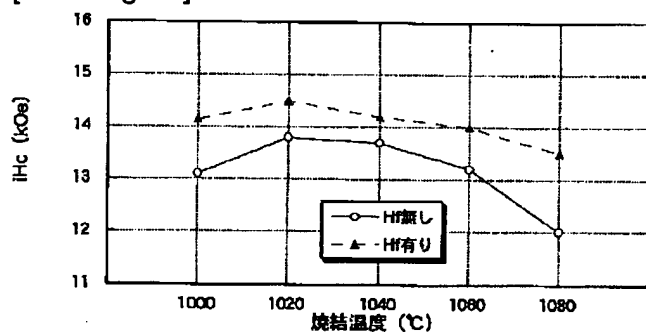
[Drawing 13]



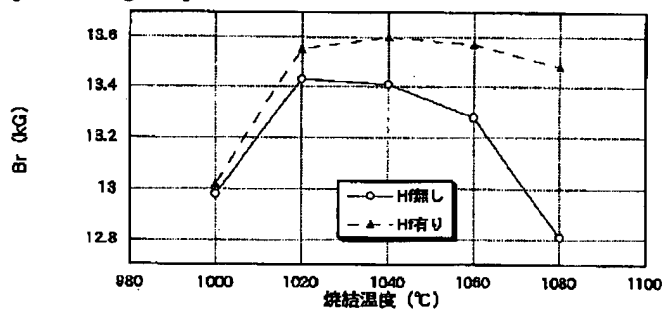
[Drawing 14]



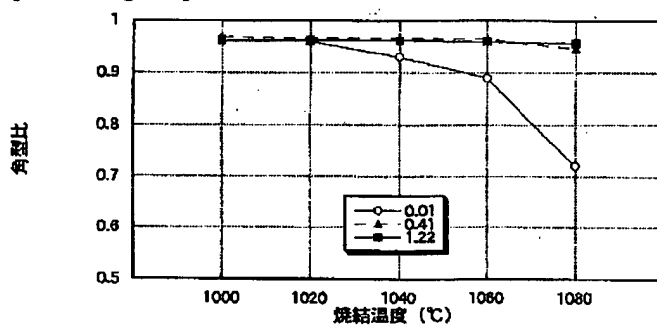
[Drawing 15]



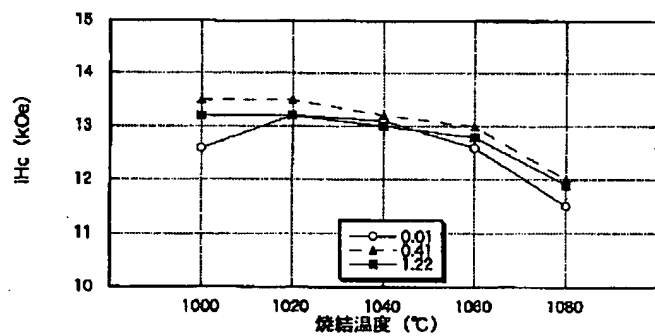
[Drawing 16]



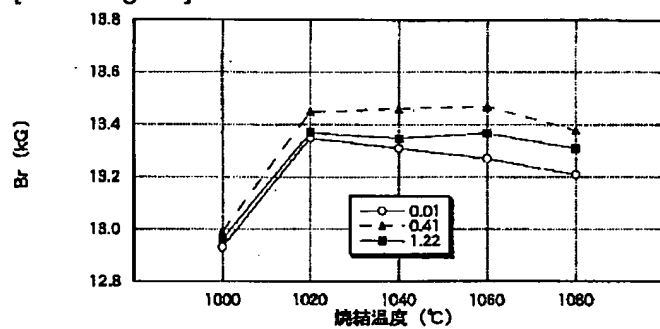
[Drawing 17]



[Drawing 18]

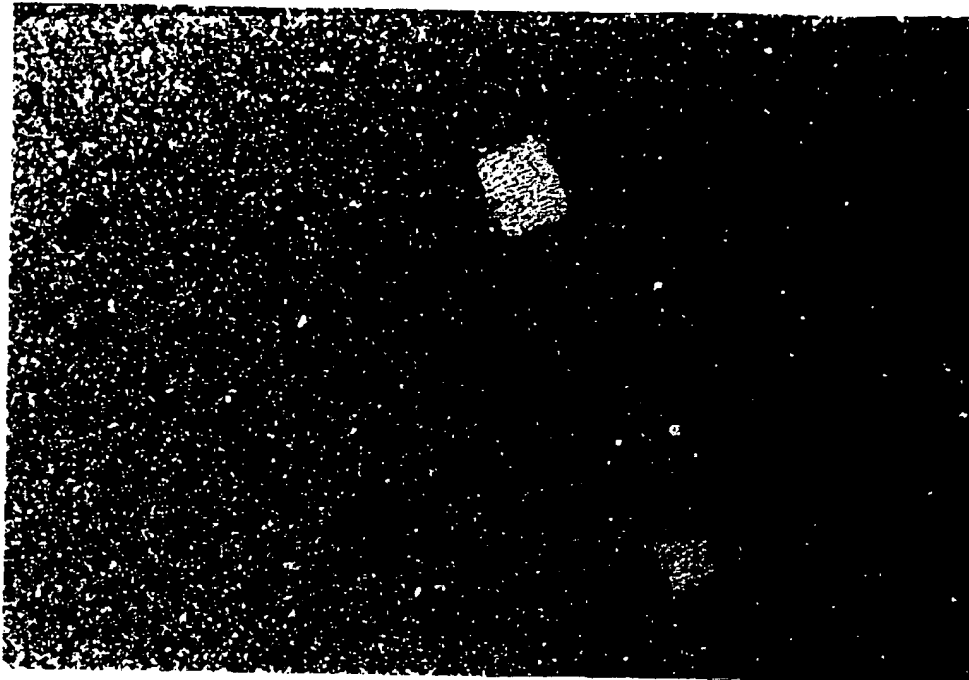


[Drawing 19]

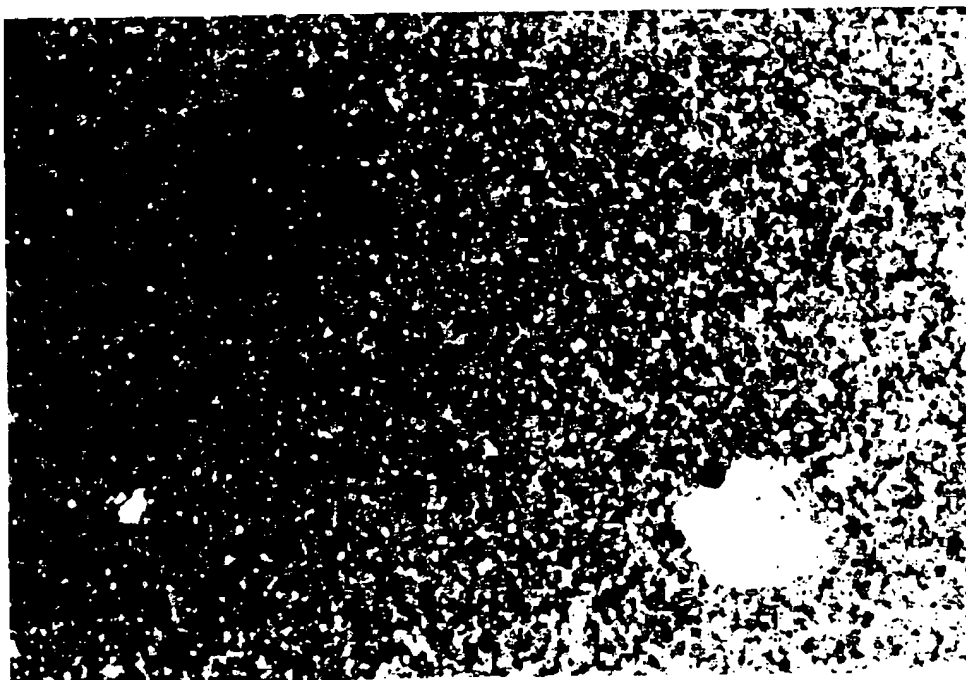


[Drawing 20]

(a)



(b)



[Translation done.]